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RESEARCH AND DEVELOPMENT OF TANTALUM- AND TUNGSTEN-BASE ALLOYS

Prepared by

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Final Report

27 June 1958 through 26 March 1961

Westinghouse Research Laboratories
Pittsburgh 35, Pennsylvania

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ABSTRACT

The effects of alloying upon the properties of tantalum and tungsten have been examined in considerable detail. A 20-gram button survey was made of the Ta-W-Hf and Ta-W-Re ternary systems to determine hardness, fabricability, oxidation resistance, and microstructure as a function of composition. Two areas were chosen for further development on a larger scale - the Ta-rich corner containing less than 10% of Hf and W, and the W-rich corner containing less than 10% of Ta and Re. Relatively little effort was expended on the scale-up of the W-base alloys. The effects of substituting or adding Ti, Zr, V, Mo, Cb and Cr into Ta- and W-base alloys were also examined by the same techniques used to examine the Ta-W-Hf-Re alloys. A few Ta-base alloys were chosen from this group for scale-up to larger sizes.

The preparation of 5 to 10 pound ingots of Ta- and W-base alloys presented a serious problem. After considerable effort had been expended, a satisfactory technique was worked out for melting and fabrication of Ta-base alloys. Fabrication of W-base alloys has not yet been placed on a routine basis.

Ta-base alloys were consumably arc melted from pressed and sintered electrodes using an AC power supply. The melting current was 2800 amperes at a voltage setting of 20 volts. The alloys were then impact extruded at

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1700°C ~~using~~ with a Dynapak ~~high energy rate~~ machine, ~~using a ratio of 4 to 1~~. The resulting sheet bar was then rolled at 1200°C to about 100 mil sheet. A stainless steel can ~~was used for~~ oxidation protection during this last working step.

The mechanical properties of the Ta-base alloys were determined ~~at temperatures~~ from -320°F to 3000°F on 50 mil sheet specimens, ~~machined from the 100 mil strip~~. The alloys in general possess a remarkable combination of excellent low temperature ductility and substantial high temperature strength. Probably the best alloy developed was the Ta-8W-4Hf alloy which had 32,000 psi ultimate tensile strength and 30,000 psi yield strength (0.2% offset) at 2700°F and had 11% elongation and 16% reduction in area at -320°F. The strengths of these alloys at relatively moderate temperatures were also exceptional; for example, the Ta-8W-4Hf alloy had a 91,000 psi ultimate tensile strength at 2200°F.

The Ta-W-Hf alloys as a class showed outstanding strengths. The substitution of Mo for W did not seriously decrease the strength of these alloys. However, the substitution of Cb for either Hf or W lowered the elevated temperature strength markedly.

A Ta-base alloy containing 2% W and 2% Re was also studied. Its properties were quite similar to the Ta-W-Hf alloy containing equivalent amounts of alloying elements.

The Ta-base alloys produced and tested in the early stage of development reported here had elevated temperature strengths competitive with the best refractory alloys presently available. At the same time, ductilities at room and subzero temperatures were quite high. Fabrication of these alloys into strip did not present any insuperable difficulties. The production of Ta-base alloys possessing truly outstanding properties appears to be a straightforward problem in alloy development.

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I. INTRODUCTION

Rapid technological advances during the past decade in the fields of aircraft, missile and atomic energy development have presented serious materials challenges to equipment designers and fabricators. In addition to the necessity for operation in extremely high temperature environments, such materials must possess high strength, be weldable, have a reasonably long life and also be able to withstand the deleterious effects of various conditions such as variable stresses, oxidation, thermal cycling, particle erosion, radiation, etc. Desirable properties of these materials must be balanced in such a manner as to produce reliable components to meet the design and economic factors which must be considered.

As required operating temperatures for these applications have advanced beyond 2000°F, the conventional iron, nickel and cobalt base alloys have become unsuitable for use because of rapid loss of strength above 1800°F. Emphasis now has been directed to the refractory metals with melting points above 4000°F in an effort to overcome present limitations. The more common refractory metals which have been under extensive investigation for a number of years are columbium, molybdenum, tantalum and tungsten. The primary goals of research and development on these materials have been to produce alloys possessing high strength in the temperature range of 2000°-3500°F which can be fabricated into useful shapes and produce alloys with sufficient inherent oxidation resistance, or alloys which can be effectively protected by suitable coatings, to operate within this temperature range without premature failure of parts.

Only limited success has been achieved to date in efforts to develop one class of materials having all the desired properties, but promising compositions have been developed in the different refractory metal systems which lead to the conclusion that further concentrated work likely will result in the solution of the major problems now being encountered. This in turn would lead to a wide area of application for the refractory metals which would not be challenged seriously by potentially competitive materials such as ceramics and cermets. By increasing the maximum temperature at which equipment components

can operate, increased efficiency and smaller packages will result. This is a factor of considerable importance in all aerospace applications where weight penalties are to be avoided, such as thermionic power generators or space radiation heat exchangers.

Molybdenum was the first refractory metal to be investigated on a scale whereby large arc-melted ingots and sizeable quantities of sheet and bar stock could be produced. Prior to this, most of the effort on refractory metals had been confined to powder metallurgy production of wire and small parts for application in the lamp, electronic and surgical fields. Alloy development has been continuous for approximately ten years, and there are several alloys commercially produced for specialized high temperature uses in the range 1800°F-2500°F. These alloys are quite difficult to fabricate and depend for their strength on extensive work-hardening below the recrystallization temperature. No truly heat-treatable composition has been developed, and oxidation resistance of all alloys is extremely poor.(1) Reasonable progress has been made in developing coatings for surface protection, but much work remains to be done.

Columbium has been studied seriously for the last five years. Since columbium is an intrinsically ductile material, with a melting point only slightly lower than that of molybdenum, it was believed that fruitful alloy research could be conducted. The oxidation resistance of pure columbium at elevated temperatures, although poor, is much better than that of molybdenum. Developments to the present time indicate that columbium alloys can be produced to meet required strength levels in the range 1800°F-2400°F by a combination of solid-solution and dispersion strengthening.(2)(3) Again, it appears that suitable coatings will be mandatory to permit satisfactory use of these alloys in projected environments.

Tungsten has generated interest in the last two or three years with the development of powder metallurgy techniques capable of producing large billets and with the adaptation of consumable electrode vacuum arc melting to the manufacture of ingots. Major effort has been expended in consolidation of pure tungsten and evaluation of physical and mechanical properties of the pure metal at elevated temperatures. Data on tungsten alloys are meager at

the present time although some results have been reported on the W-Ta, W-Mo, W-Cb and W-Re systems.[4] Due to the extreme melting point of tungsten, highest of all the elements, the possible alloying combinations which could be produced by any conventional means probably will be severely limited. This is due to the fact that retention of most lower melting point materials during processing of tungsten, especially in a vacuum environment, may be difficult. However, there are a sufficient number of possibilities available to make extended effort worthwhile. Alloys of tungsten would be advantageous in the temperature range 2500°F-4000°F, since their strength-density ratios would not be attractive at lower temperatures. Theoretically, these alloys should possess the highest temperature capabilities of any metal except for the fact that poor oxidation resistance is again a problem.

Tantalum alloy development has received less attention than alloy development in molybdenum and columbium and only recently has more interest been expressed in the possibilities of tantalum-base alloys. Tantalum is similar in many of its properties to columbium, being even more ductile at room and sub-zero temperatures, but it possesses a melting point almost 1000°F higher than columbium and a room temperature modulus of elasticity of 27×10^6 psi vs. 15×10^6 psi for columbium. Its oxidation resistance is poor, similar to that of columbium, but catastrophic oxidation as in molybdenum does not occur at low temperatures. Tantalum, like columbium, possesses moderate strength at room temperature, but strength decreases more slowly at elevated temperatures when compared to most metals. The alloying of tantalum with high melting point solid solution additions has shown promise of producing families of tantalum-base materials which will possess good strength in the temperature range 2500°F-3500°F, combined with a fair degree of weldability and formability. Coatings would be required for exposure to oxidizing media at projected use temperatures.

The properties of pure tantalum and pure tungsten have been under continuous investigation for many years because of the use of these metals in the lamp and electronic industries. Considerable data are available in several State-of-the-Art reference works.[4][5][6] However, there is a paucity of information on the alloys of these metals since significant effort has been

expended only in the last two or three years, and that by a limited number of research organizations. It is known that tungsten alloys containing additions of tantalum, columbium, molybdenum and rhenium have been produced in ingots up to 7" in diameter by both arc melting and powder metallurgy techniques, and some mechanical property data have been reported, generally on laboratory scale samples.[7][8][9] The difficulties associated with the consolidation and fabrication of tungsten and its alloys are formidable, and the surface has been merely scratched in the development of this metal. Tantalum and its alloys have been investigated recently to a considerable extent by Battelle Memorial Institute, and interesting information on mechanical properties and oxidation resistance has been reported.[10] Molybdenum and tungsten can be alloyed with tantalum to form alloys with a combination of high temperature strength and low temperature ductility. Interstitial element additions are capable of imparting further strengthening, particularly if accompanied by additions of reactive elements such as titanium, zirconium or hafnium.

The research carried out to date on alloys of tungsten and tantalum has been concerned primarily with property measurements on a laboratory basis and not with methods of producing large quantities of bar and sheet for fabrication into hardware items. Since the ability to manufacture acceptable products which will meet required specifications is the desired goal of any alloy development program, it is necessary that scale-up activities be conducted on materials which appear promising from small-scale screening studies. In turn, the screening studies themselves should be conducted in a realistic fashion to eliminate possible compositions which, by logical reasoning, could be assumed not amenable to a larger pilot plant operation. The procedures chosen for production development should be as straightforward and uncomplicated as possible, lending themselves to existing techniques wherever feasible. Alloys carried through the various phases of processing should be expected to furnish a reasonable yield and thus make the economics of the process justifiable. Finally, finished products should be uniform in quality and should show reproducible results for tests obtained from one lot of the same composition.

Since little work had been reported on the development of tantalum and tungsten base alloys, an investigation was undertaken to determine the general

alloying characteristics of these metals with the objectives of improving high temperature strength and developing scale-up techniques for production of promising compositions in bar and sheet form. It was believed that tantalum and tungsten, with extremely high melting points, could be made the bases of alloy systems possessing strengths in the range 2000°-3500°F greater than those obtainable from presently available metal alloys. At these temperatures, strength-weight relationships might be attractive despite the high densities of tantalum and tungsten.

The work to be described was sponsored by the Department of the Navy, Bureau of Naval Weapons. The general approach consisted of three distinct phases of effort. Phase I involved a screening study of binary and ternary systems of tantalum and tungsten bases with additions of rhenium and hafnium. Rhenium was selected as an alloy addition because of its high melting point, extended solid solubility in both tungsten and tantalum, and because little information was available on its strengthening effects on high melting point metals. Hafnium was selected because of the demonstrated ability of the reactive metals to strengthen refractory metal alloys when present in small percentages. Titanium and zirconium had been investigated to a considerable extent in molybdenum and columbium alloys, while hafnium had received less attention and could be expected to demonstrate similar properties when alloyed with tantalum. It was believed that the two ternary systems Ta-W-Hf and Ta-W-Re could contain alloy compositions which would possess the desired elevated temperature properties. Phase III consisted of another screening study of binary and ternary alloys of tungsten and tantalum. In this study the elements zirconium and titanium were substituted for hafnium; vanadium substituted for tantalum in high tungsten compositions; and molybdenum and chromium substituted for tungsten in high tantalum compositions. These elements were selected because they were in the refractory or reactive metal groups IVa, Va, VIa of the periodic table, had compatible crystal structures, high melting points and possessed other characteristics similar to those of the alloy base metals. Phase II was a scale-up operation whereby a number of promising compositions developed in Phases I and III were produced in the form of arc-melted ingots, reduced to strip and tested for mechanical properties.

The experimental procedure was selected to employ methods of consolidation, working and testing which could be performed in the laboratory. A variety of specialized equipment was available and employed during the course of the program. The more important items are described in some detail in Appendix A. All the procedures followed were kept as simple as possible to permit translation into a production practice at a later date with a minimum of effort.

It was planned originally to prepare alloys of Phases I and III in the levitation melting unit, but the equipment was unable to raise the materials to their melting points. Consequently, the non-consumable arc melting furnace was used to prepare all compositions for screening. The vacuum hot hardness tester was used to obtain hot hardness data on annealed-cast buttons. Elevated temperature heat treatments of buttons were conducted in the high temperature resistance heated vacuum furnace and in the induction heated vacuum furnace. Cold rolling was conducted on a laboratory mill and hot forging on a pneumatic forging hammer. Phase II alloy ingots were made by consumable electrode vacuum arc melting. For tantalum alloy electrodes, additions in a powder or rod form were pressed together with high purity tantalum powder into rectangular bars in a 1000-ton press. Tungsten alloy electrodes were made by attaching alloy additions in the form of rod and wire to sintered and swaged high purity tungsten bar. Electrodes were melted in the vacuum arc furnace using AC or DC power. The ingots produced were conditioned to billets and extruded in the Dynapak high velocity extrusion press at high temperatures. The extruded shape was a rectangular sheet bar which were then warm rolled to strip in protective stainless steel cans. The strip material was conditioned to .050" finished thickness and longitudinal tensile test specimens were prepared for both high and low temperature testing. The test data were evaluated and recommendations were made for the direction future work should take.

II. RAW MATERIALS

The tantalum used in this investigation was procured from two sources. High purity tantalum powder (-12 + 100 mesh) was obtained from National Research Corporation. The chemical analysis furnished by the manufacturer was as follows:

NRC Pure Tantalum Powder (Type M-Lot MG-109)

C	25 ppm	Fe	50 ppm
O	311 ppm	Mo	25 ppm
N	35 ppm	Ni	98 ppm
H	30 ppm	Si	170 ppm
Al	50 ppm	Ti	10 ppm
Cr	39 ppm	Nb	63 ppm
Cu	50 ppm	Na	75 ppm

High purity tantalum dendrites were purchased from the Union Carbide Metals Co. to conform to the following analysis:

Union Carbide Pure Tantalum Dendrites

C	40 ppm maximum
O	200 ppm maximum
N	---
H	180 ppm maximum
Ni	110 ppm maximum
Fe	240 ppm maximum

Dendrites were used for initial button melting studies in Phase I and Phase III. The powder was pressed into consumable electrodes for ingot manufacture in Phase II.

Tungsten was employed in three forms. High purity tungsten powder (-100 +150 mesh) and sintered tungsten bar were supplied by the Lamp Division of Westinghouse. They were used in Phase I and Phase III button melt screening studies and for Phase II alloy additions. Sintered and swaged round bars of high purity tungsten were obtained from the General Electric Co. These bars

were of 5/8" diameter and 30" length, with a density at least 95% of the theoretical value. Such bars were used as tungsten-base consumable electrodes in Phase II scale-up operations. No analyses were furnished by the manufacturers, so representative samples were arc-melted and analyzed for interstitial elements. The following results were reported.

	Pure Tungsten	
	C	O
Westinghouse Sintered Tungsten Bar	36 ppm	10 ppm
Westinghouse Tungsten Powder	--	6 ppm
General Electric Swaged Tungsten Bar	26 ppm	3 ppm

Rhenium was obtained from Chase Brass and Copper Co. in the form of high purity sintered bar. Rhenium powder was obtained from the Varlacoid Co. The bar dimensions were 1/4" x 1/4" x 6" long. These bars were subsequently cold swaged to desired diameters for use as alloy additions in the scale-up Phase II of the program. Intermediate vacuum annealing at 1600°C was necessary after each 10% of cold reduction in order to work the material without occurrence of fracture. Powder was arc melted, rolled to sheet, and sheared. It was then used for alloy additions to button melts in Phase I and Phase III. Arc-melted samples were analyzed for interstitial elements. Results were as follows:

	Pure Rhenium	
	C	O
Sintered Rhenium Bar	93 ppm	3 ppm
Sheared Rhenium Sheet	60 ppm	6 ppm

Hafnium was delivered by the Bettis Atomic Power Laboratory of Westinghouse in the form of iodide crystal bar. Some bar material was rolled to sheet, which was then sheared and used for alloy additions in Phase I and III. Other bars were reduced in size by swaging to produce desired lengths and diameters of rod for alloy additions in earlier stages of the consumable electrode melting

studies. In later work the hafnium crystal bar was hydrided, crushed to fine powder, and added to pressed electrodes as a hydride. The hydrogen was later removed during a vacuum sintering operation. Analysis of an arc melted sample of this material showed the following interstitial levels:

Pure Hafnium Crystal Bar

C	190 ppm
O	250 ppm
N	10 ppm

Molybdenum was used in the form of cuttings from arc melted sheet produced by Climax Molybdenum Corp. and also as a powder manufactured by Westinghouse. The sheet material was used in Phase III screening studies, and the powder for Phase II alloy additions to consumable electrodes.

Vanadium was furnished by Union Carbide Metals Co. in the form of -20 mesh powder. Typical supplier's analysis of the material was as follows:

Pure Vanadium Metal Powder

C	460 ppm
O	800 ppm
N	570 ppm
H	10 ppm

This powder was used in both button melting and scale-up operations.

Electrolytic chromium platelets were supplied by Union Carbide Metals Co. These platelets were crushed in a mortar to produce fine powder which was then used as an alloy addition.

Titanium was obtained from the Foote Mineral Co. as iodide crystal bar and conformed to the following specification:

Pure Titanium Crystal Bar

C	10 ppm	Cr	20 ppm
O	20 ppm	Al	50 ppm
N	20 ppm	Si	50 ppm
Zr	500 ppm	Mg	30 ppm
Fe	20 ppm		

Zirconium also was obtained from Foote Mineral Co. as iodide crystal bar and met this specification:

Pure Zirconium Crystal Bar

C	< 10 ppm	Ti	1000 ppm
O	<100 ppm	Ni	100 ppm
N	<100 ppm	Si	100 ppm
Hf	2.4%	Al	100 ppm
Fe	1000 ppm		

All raw materials, except fine powders, were cleaned in an acetone bath and thoroughly dried before melting. This was done to ensure the removal of dirt and grease which could have been present on surfaces.

III. EXPERIMENTAL PROCEDURE AND RESULTS

A. PHASE I - PRIMARY SCREENING STUDIES -- The literature was surveyed for phase diagram and structure information and for physical and mechanical property data on the Ta-W-Re-Hf alloys. Results of this survey revealed the following information on the individual systems.[11-18]

Ta-W --- Ta and W have been reported to be soluble in all proportions. The change in lattice parameter with composition showed only a slight negative deviation from Vegard's Law. Initial additions of W to Ta increased the hardness rapidly. At about 50% W the hardness reached a level comparable to pure W and further additions did not cause increased hardening. Additions of up to 10% W in Ta increased the room temperature tensile strength in an almost linear manner. The strength of the 10% W alloy was about 2-1/2 times that of pure Ta. Tensile elongation at room temperature decreased with increasing W content. The work hardening rate of Ta was increased by W additions and additions of more than 10% W made Ta difficult to work at room temperature. Attempts to fabricate these alloys at 500°C did not prove successful. The addition of 10% W to Ta raised the apparent recrystallization temperature 50°C above that for pure Ta.

Ta-Hf --- Only one reference to this alloy system could be found in the literature. An alloy having the composition Ta_2Hf could not be crushed or fractured, possibly indicating appreciable ductility at room temperature. X-ray analysis indicated the structure to be composed of both body-centered-cubic and close-packed hexagonal phases. Recent unpublished work at the Bureau of Mines has established a tentative phase diagram, showing a miscibility gap at temperatures below about 1500°C.

Ta-Re --- Re has been reported soluble in Ta up to 48-50% Re. At higher Re contents a σ-type and a χ-type phase were found.

No data are available on the physical or mechanical properties of alloys in this system.

W-Re --- It has been reported that W will dissolve approximately 37% Re. Higher Re additions caused the formation of a σ-type phase and a χ-type phase. The solubility decreased from 37% at the peritectic temperature of 3000°C to about 28% at 1600°C. This was accompanied by an increase in the composition range of the adjacent two phase body-centered-cubic and σ-phase region. The addition of Re improved the room temperature ductility of W, as shown by the amount of reduction on rolling that was possible before cracking was observed. The improvement in workability increased with increasing Re content up to about 30% Re, after which it decreased rapidly. This rapid decrease in workability probably was associated with the formation of the σ-phase. The maximum room temperature reduction for the 30% Re alloy by rolling before observed cracking was 12%, compared to 0% for pure W. A W-35 Re alloy which was reduced 40% by cold rolling (specimen contained cracks) retained its hardness quite well to 800°C. The room temperature hardness of this material was 575 VHN, while at 800°C the hot hardness was 350 VHN. Comparable hardness values for pure W at the above temperatures were 450 VHN and 77 VHN respectively.

Ta-W-Hf --- No information concerning this ternary system was found in the literature.

Ta-W-Re --- Some data have been reported recently concerning the solid solution field of the Ta-W-Re ternary system. For example, an alloy of composition 35Ta-25W-40Re had a two-phase structure (b.c.c. + σ) while alloys of 15Ta-25W-60Re and 25Ta-25W-50Re were reported as being composed completely of the σ-phase. No mechanical property data for this system were found.

Since practically no mechanical properties of the alloy systems under consideration were found in the literature survey, an elementary approach to the program was taken. Initial work was conducted on pure Ta, pure W, the binary alloys Ta-W, W-Hf, W-Re, Ta-Hf, Ta-Re and the ternary systems Ta-W-Re, Ta-W-Hf. The general screening procedure consisted of the following:

(1) Room temperature as-cast hardness
(2) Room temperature hardness after a 16 hour homogenization vacuum anneal at 2000°C.
(3) Metallographic examination of structures in (1) and (2).
(4) Cold workability by rolling at room temperature.
(5) Hot workability by forging at 1200°C.
(6) Oxidation resistance at 1200°C.
(7) Hardness at elevated temperatures.

The alloys prepared for Phase I screening tests were composed of the purest commercially available metals. No further purification was performed beyond possible solid state processes consisting of vacuum heat treatment to decrease gaseous impurities.

The raw materials were originally intended for consolidation into small alloy ingots by levitation melting as described in Appendix A. Several problems were encountered during preliminary attempts to levitation melt tantalum and tungsten, both of which possess higher melting points and greater densities than previously levitated and melted materials. A specimen of tungsten weighing 10 grams was levitated using a 10-KC power supply but could not be melted. The specimen temperature was 2200°C as measured by an optical pyrometer. A 450-KC power supply delivering 600 amperes was the best obtainable when work was initiated on the project. This current was sufficient to lift molybdenum but not the denser metals. The obvious need for higher currents necessitated enlarging the terminal plates to which the capacitors were attached so that more capacitors could be used with the existing apparatus. Currents of 800 amperes could then be obtained with these improvements.

A number of melting trials were made in vacuum. They were conducted in a two-turn coil carrying as large a current at 450-KC as could be obtained by parallel capacitor tuning with a 10 KW, 370 ampere R.F. generator. A movable "dock" consisting of a water cooled copper disc, concave downward, was placed above the top turn of the levitating coil and was used to obtain specimen stability in the coil. This "dock" replaced the reverse turns used to obtain specimen stability on previous coils. Stability was achieved in this manner without the increase in coil voltage which accompanies the use of the reverse turn technique.

Specimens of swaged rod and sintered powder compacts of tungsten weighing up to 37 grams could be floated free of the coil for a considerable length of time. Temperatures as high as 3260°C at the bottom of the specimen, and about 200°C cooler at the top, were measured. However, the specimens could not be melted. Polishing the under side of the "dock" to produce a mirror reflection did not increase the temperature obtainable.

Under these same conditions, tantalum and tantalum-hafnium compacts could be floated and partially melted; however, the specimen dripped before complete melting could be obtained. In the case of tantalum, the best solution appeared to be the use of a stronger field to hold the melt. This was tried using a three-turn coil. Pure tantalum was melted successfully in vacuum and cast into cylindrical specimens. The addition of the third turn to the melting coil did not cause breakdown in vacuum due to the higher voltage.

In regard to tungsten and its alloys, continued experimentation over a period of several months failed to produce a workable procedure for melting small ingots by the levitation method.

A common alloy preparation method was needed to prepare both tantalum and tungsten alloys in order to eliminate variables arising from the use of different melting procedures. Therefore, it was decided to abandon the levitation melting approach and concentrate on tungsten electrode arc melting of buttons in a water cooled copper hearth. A six hearth melting unit was constructed and was used throughout the screening phases of the program. The furnace is described in Appendix A.

Materials to be melted were in the forms of powder, sponge, sheared sheet or chips. 20-gram samples of nominal alloy content were compacted in a small hydraulic press to cylinders which possessed sufficient strength to remain intact when handled. The compacts were placed in the individual bowl-shaped hearths of the arc furnace. One of the hearths contained a getter button of titanium. The getter button was always melted first so as to purify the argon atmosphere in the chamber. Button alloys of tantalum or tungsten were generally melted at least twice on each side to assure homogeneity. Currents used for 20 gram melts ranged from 250 to 600 amperes, depending upon the particular alloy melted.

Melted button specimens were weighed to determine whether weight loss had occurred during the melting operation. Check chemical analyses also were conducted on representative compositions of different alloy systems. In the Phase I alloys there was no measurable loss of alloy additions during melting. This was not true for the systems studied in the Phase III work which involved addition of V, Ti and Zr to a tungsten base, or Cr to a tantalum base.

Room temperature hardnesses on as-cast specimens were obtained on a Vickers machine with a 136° diamond pyramid indenter. Flats were ground on upper and lower faces of the buttons. At least four readings were made and averaged to give each reported hardness value. The 16 hour homogenization vacuum anneals were generally carried out in the high temperature induction heating furnace described in the section on experimental equipment. Metallographic procedures for preparing microstructures are described in Appendix B attached to this report. Cold workability of specimens was observed by rolling the buttons on a small two-high laboratory rolling mill. Hot workability was determined by forging buttons on a steam hammer after heating them to 1200°C in an inert atmosphere furnace. In this case, the hammer was allowed to contact the specimen with a small, controlled degree of work so as not to impart a full hammer blow which might have destroyed the specimen entirely. Specimens were reduced approximately 50% by one hammer blow.

The results of these evaluation tests are listed in Tables I-III. All alloy compositions are reported in weight percent and were prepared by the

TABLE I. STRUCTURE AND HARDNESS OF PHASE I ALLOYS

Composition			Condition: As Arc Melted	Condition: 2000°C Homog.[1]	Composition			Condition: As Arc Melted	Condition: 2000°C Homog.
Ta			S.P.[2]-120[3]	S.P.-112	Ta	W	Hf		
W			S.P.-373	S.P.-326	88	8	4	S.P.-268	S.P.-283
Hf			S.P.-202	S.P.-275	80	16	4	S.P.-330	S.P.-348
Re			S P.-143	--	64	32	4	S.P.-470	S.P.-475
Ta	W	Hf			48	48	4	S.P.-561	S.P.-505
99	1	0	S.P.-163	S.P.-139	32	64	4	T.P.-499	T.P.-512
98	2	0	S.P.-134	S.P.-121	26	70	4	T.P.-490	T.P.-507
96	4	0	S.P.-170	S.P.-175	16	80	4	T.P.-449	T.P.-490
92	8	0	S.P.-233	S.P.-215	8	88	4	S.P.-435	S.P.-455
84	16	0	S.P.-308	S.P.-300	4	92	4	T.P.-427	S.P.-419
75	25	0	S.P.-387	S.P.-400	2	94	4	T.P.-418	S.P.-417
68	32	0	S.P.-391	S.P.-413	0	96	4	T.P.-363	S.P.-361
50	50	0	S.P.-526	S.P.-443	95	0	5	S.P.-172	S.P.-199
36	64	0	S.P.-517	S.P.-485	92	0	8	S.P.-222	S.P.-227
25	75	0	S.P -420	S.P.-386	90	2	8	S.P.-237	S.P.-231
16	84	0	S.P.-400	S.P.-396	88	4	8	S.P.-252	S.P.-294
8	92	0	S.P.-404	S.P.-419	84	8	8	S.P.-289	S.P.-353
4	96	0	S.P.-396	S.P.-396	76	16	8	S.P.-493	S.P.-440
2	98	0	S.P.-402	S.P.-391	60	32	8	S.P.-473	S.P.-509
0	99-1/2	1/2	S.P.-368	S.P.-361	32	60	8	S.P.-540	S.P.-591
99	0	1	S.P.-133	S.P.-98	16	76	8	T.P.-557	T.P.-496
0	99	1	S.P.-371	S.P.376	8	84	8	T.P.-422	T.P.-442
98	0	2	S.P.-147	S.P.-124	4	88	8	T.P.-400	T.P.-413
96	2	2	S.P.-183	S.P.-213	2	90	8	T.P.-485	T.P.-490
94	4	2	S.P.-202	S.P.-200	0	92	8	T.P.-398	T.P.-433
90	8	2	S.P.-252	S.P.-257	90	0	10	S.P.-202	S.P.-220
82	16	2	S.P.-330	S.P.-316	45	45	10	T.P.-554	S.P.-578
66	32	2	S.P.-454	S.P.-442	84	0	16	S.P.-281	S.P.-229
49	49	2	S.P.-490	S.P.-465	82	2	16	S.P.-291	S.P.-317
32	66	2	S.P.-502	S.P.-516	80	4	16	S.P.-312	S.P.-362
16	82	2	S.P.-423	S.P.-439	76	8	16	S.P.-389	S.P.-386
8	90	2	S.P.-398	S.P.-390	68	16	16	S.P.-415	S.P.-457
4	94	2	S.P.-348	S.P.-388	52	32	16	T.P.-557	T.P.-566
2	96	2	S.P.-391	S.P.-362	32	52	16	T.P.-665	T.P.-689
0	98	2	S.P.-329	S.P.-373	16	68	16	T.P.-618	T.P.-605
96	0	4	S.P.-161	S.P.-186	8	76	16	T.P.-561	T.P.-672
94	2	4	S.P.-191	S.P.-232	4	80	16	T.P.-622	T.P.-645
92	4	4	S.P.-211	S.P.-243	2	82	16	T.P.-669	T.P.-719
					0	84	16	T.P.-618	T.P.-685

TABLE I. (Cont'd)

Composition Ta-W-Hf			Condition: As Arc Melted	Condition: 2000°C Homog.(1)	Composition Ta	W	Re	Condition: As Arc Melted	Condition: 2000°C Homog.
80	0	20	S.P.-272	S.P.-286					
60	20	20	T.P.-438	T.P.-504	4	92	4	S.P.-336	S.P.-330
40	40	20	T.P.-557	S.P.-511	2	94	4	S.P.-329	S.P.-337
50	25	25	T.P.-550	T.P.-552	0	96	4	S.P.-312	S.P.-298
25	50	25	T.P.-675	T.P.-832	92	0	8	S.P.-344	S.P.-361
35	35	30	T.P -631	Melted-744	84	8	8	S.P.-429	S.P.-411
68	0	32	S.P.-366	T.P.-446	76	16	8	S.P.-475	S.P.-434
66	2	32	S.P.-360	T.P.-579	60	32	8	S.P.-508	S.P.-497
64	4	32	S.P.-362	--	46	46	8	S.P.-564	S.P.-529
60	8	32	S.P.-376	--	32	60	8	S.P.-446	S.P.-419
52	16	32	S.P.-478	--	16	76	8	S.P.-406	S.P.-383
16	52	32	T.P.-648	T.P.-885	8	84	8	S.P.-371	S.P.-356
8	60	32	T.P.-912	T.P.-938	4	88	8	S.P.-338	S.P.-330
4	64	32	T.P.-856	T.P.-928	0	92	8	S.P.-298	S.P.-290
0	68	32	T.P.-982	T.P.-1070	84	0	16	S.P.-523	S.P.-517
30	30	40	T.P.-652	Melted-734	80	4	16	S.P.-537	S.P.-575
50	0	50	S.P.-389	T.P.-546	76	8	16	S.P.-550	S.P.-528
42	8	50	S.P.-432	--	68	16	16	S.P.-598	S.P.-562
34	16	50	S.P.-502	--	52	32	16	S.P.-610	S.P.-663
25	25	50	T.P.-575	Melted	42	42	16	S.P.-520	S.P.-507
16	34	50	T.P.-648	--	32	52	16	S.P.-514	S.P.-488
8	42	50	T.P.-705	--	16	68	16	S.P.-470	S.P.-451
20	20	60	T.P.-517	Melted	8	76	16	S.P.-444	S.P.-430
Ta	W	Re			4	80	16	S.P.-434	S.P.-408
99	0	1	S.P.-134	S.P.-158	0	84	16	S.P.-374	S.P.-388
0	99	1	S.P.-358	S.P.-333	76	0	24	S.P.-626	S.P.-599
98	0	2	S.P.-189	S.P.-194	68	8	24	S.P.-638	S.P.-620
96	2	2	S.P.-232	S.P.-189	60	16	24	S.P.-535	S.P.-555
4	94	2	S.P.-336	S.P.-354	52	24	24	S.P.-540	S.P.-478
2	96	2	S.P.-364	S.P.-352	38	38	24	S.P.-529	S.P.-527
0	98	2	S.P.-343	S.P.-335	24	52	24	S.P.-525	S.P.-523
96	0	4	S.P.-239	S.P.-252	8	68	24	S.P.-478	S.P.-488
94	2	4	S.P.-269	S.P.-246	4	68	28	T.P.-422	S.P.-454
92	4	4	S.P.-304	S.P.-274	2	68	30	T.P.-425	S.P.-452
88	8	4	S.P.-325	S.P.-307	68	0	32	S.P.-614	S.P.-689
80	16	4	S.P.-387	S.P.-368	34	34	32	T.P.-662	S.P.-518
64	32	4	S.P.-467	S.P.-440	16	52	32	T.P.-606	T.P.-565
32	64	4	S.P.-467	S.P.-415	8	60	32	T.P.-473	T.P.-495
16	80	4	S.P.-362	S.P.-353	4	64	32	T.P.-540	S.P.-504
8	88	4	S.P.-366	S.P.-348	2	66	32	T.P.-478	T.P.-511
					0	68	32	T.P.-514	T.P.-558
					50	0	50	T.P.-1099	T.P.-
					36	0	64	S.P.-1337	--

(1) 16 Hours at 2000°C Homogenization Anneal
(2) S.P. - Single Phase, T.P. - Two or more Phase
(3) Hardness in VHN

TABLE II

WORKABILITY OF PHASE I ALLOYS

Composition			Rolled at 25°C	Forged at 1200°C
Ta	W	Hf		
99	1	0	Excellent	-
98	2	0	"	-
96	4	0	"	-
92	8	0	"	-
84	16	0	"	-
68	32	0	Poor	Good
99	0	1	"	"
98	0	2	Excellent	-
96	0	4	"	-
95	0	5	Good	-
92	0	8	Poor	Good
90	0	10	"	"
84	0	16	"	"
80	0	20	"	Fair
68	0	32	"	Good
96	2	2	-	"
92	4	4	-	"
84	8	8	-	"
68	16	16	-	Fair
34	34	32	-	"
			-	Poor

TABLE III

OXIDATION RESISTANCE OF PHASE I ALLOYS[1]

Composition (%) Ta	W	Hf	Re	Weight Gain $mg/cm^2/hr.$	Comments on Scale
100	-	-	-	105	Porous, Non-adherent
-	100	-	-	77[2]	Thick, Non-adherent
68	32	-	-	59[2]	Thick, Adherent
32	68	-	-	21[2]	Thick, Very adherent. Also a Granular, Non-adherent Layer
68	-	32	-	39[2]	Med. Thick, Very Adherent
-	68	32	-	14[2]	Spalled
68	-	-	32	25	Granular, Non-adherent. Also Thin Fused Layer
-	68	-	32	89	Thick, Non-adherent
32	-	68	-	10	Thin, Very Adherent
-	32	68	-	17[2]	Granular, Non-adherent
34	33	-	33	24[2]	Granular, Non-adherent. Also Thin Fused Layer
34	33	33	-	18	Thin, Very Adherent
92	4	4	-	101	Porous, Non-adherent
84	8	8	-	24	Portion Spalled, Portion Very Adherent
69	26	5	-	64	Thick, Non-adherent
48	48	4	-	26	Thin, Spalled
36	60	4	-	7.5[3]	

(1) Specimens held 1 hr. at 1200°C in flowing air.

(2) Calculated from weight loss after scale removal.

(3) Scale could not be removed. Value probably low.

nonconsumable electrode arc melting technique. Annealing treatments were 16 hours at 2000°C unless otherwise specified. The compositions prepared are shown in Fig. 1 which is a double ternary plot of the Ta-W-Hf and Ta-W-Re systems.

The data in Table I are illustrated in four isothermal sections of the two ternary systems. Figures 2 and 3 are the as-cast and as-annealed at 2000°C sections of the Ta-W-Hf system. Figures 4 and 5 are similar sections in the Ta-W-Re system. Plotted on these diagrams are the solubility limits and the lines of equal hardness in the various conditions. The structures of individual alloys are also shown. The four sections will be discussed individually.

(1) Ta-W-Hf, As Arc Melted, Fig. 2

The solubility of Hf in Ta is greater than 50%. The hardness increases smoothly from 120 VHN at pure Ta to 389 VHN at 50% Hf. The addition of 4% Hf to W results in the precipitation of a second phase, presumably W_2Hf. The hardness increases rapidly through the two phase area, with the single phase W_2Hf having a hardness of about 1000 VHN. Ta and W form a continuous series of solid solutions. The hardness of both Ta and W is increased by alloying with the other element. The addition of W increases the hardness smoothly to a value of 526 VHN at 50% W. The addition of 2% Ta increases the hardness of W from about 335-365 VHN to 400 VHN. Further additions do not increase the hardness appreciably until a level of more than 16% Ta is reached. This behavior is also noted in the ternary alloys, where a small addition of 2% Ta to a W-4% Hf alloy increases the hardness 50 VHN, while a further 2% increase of Ta only increased the hardness by 10 VHN. While the microstructures do not indicate the presence of a second phase in these low Ta alloys a dispersed phase (possibly TaC) is believed responsible for this behavior. The solubility of Hf in Ta-W alloys increases with increasing Ta content. In general, hardness increases as the W_2Hf composition is approached.

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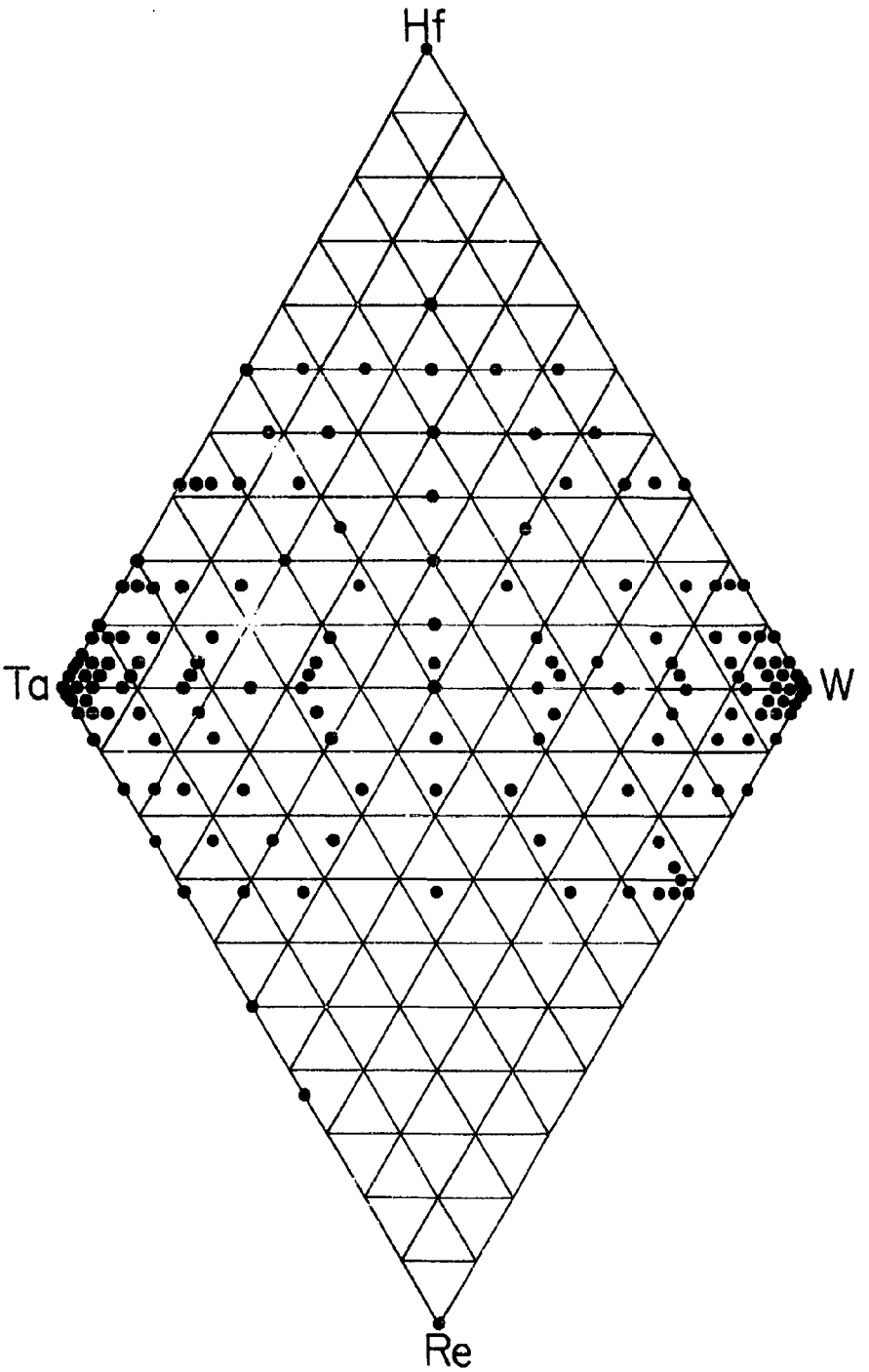

Fig. 1 - Alloys prepared in the Ta - W - Re - Hf system

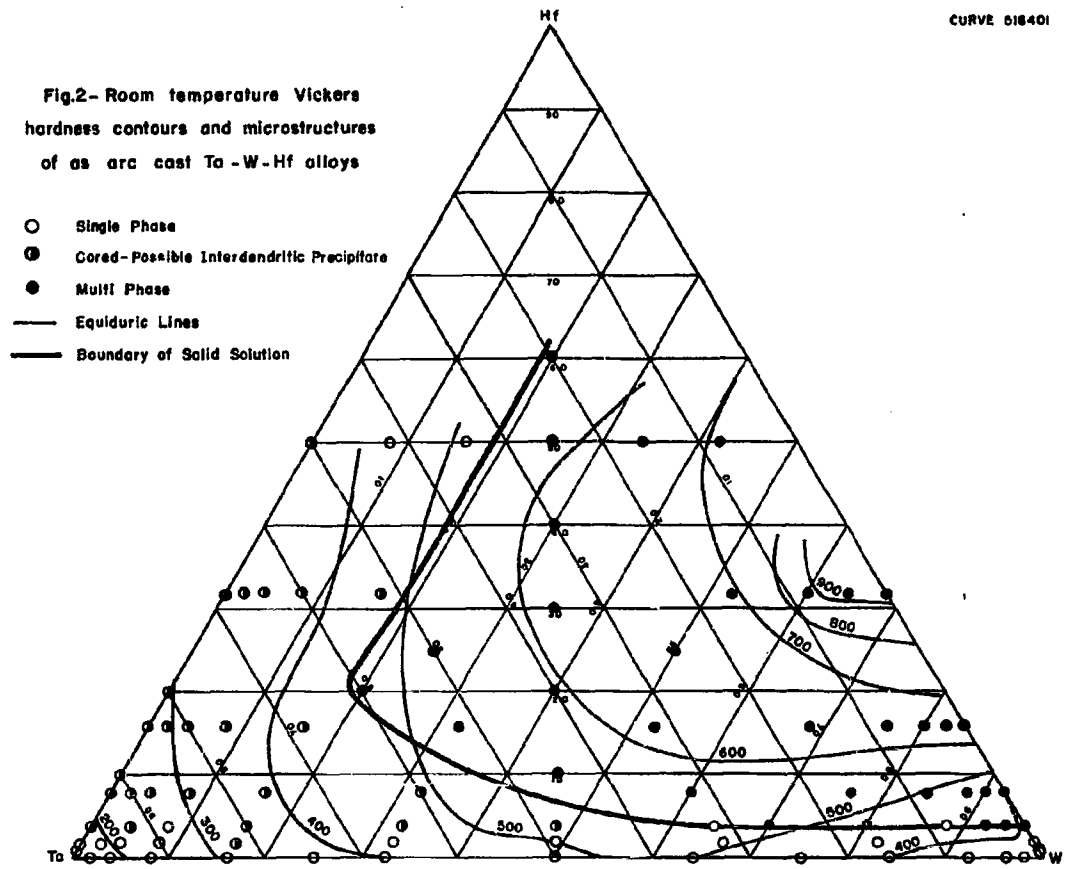

Fig.2- Room temperature Vickers hardness contours and microstructures of as arc cast Ta - W - Hf alloys

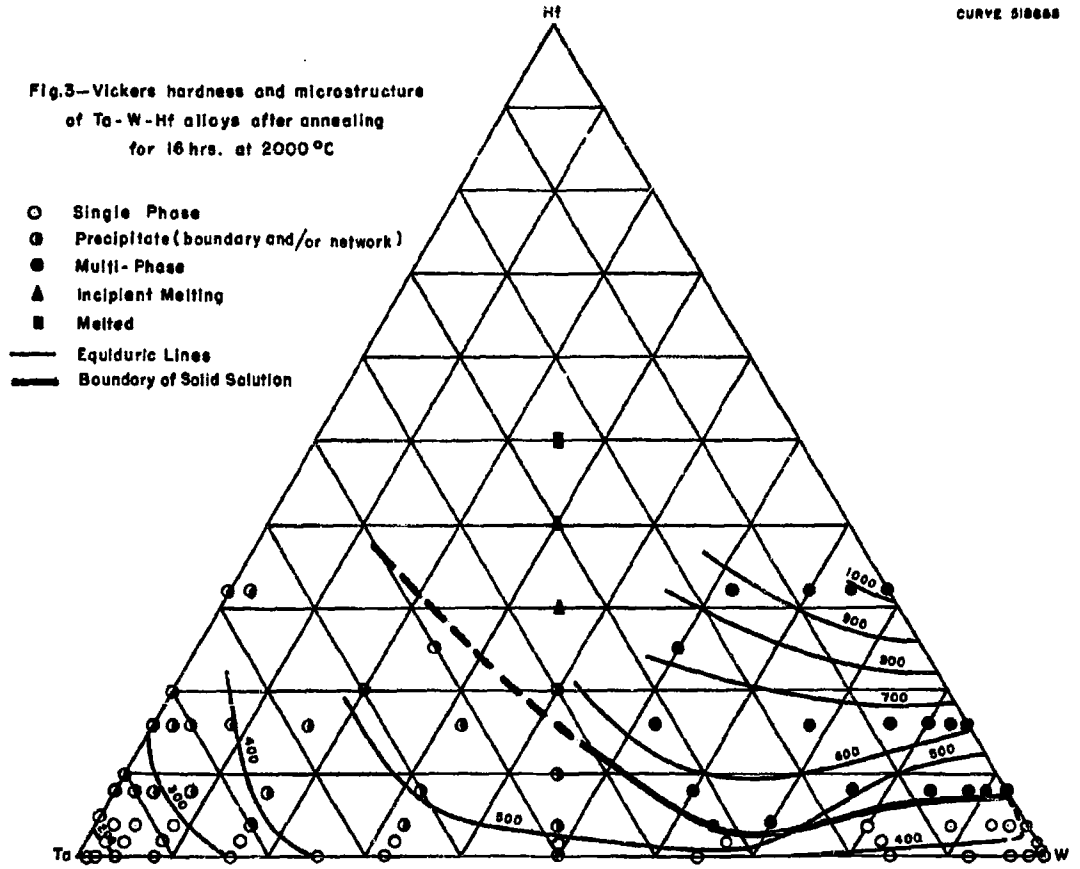

Fig.3—Vickers hardness and microstructure of Ta-W-Hf alloys after annealing for 16 hrs. at 2000°C

- ○ Single Phase
- ◐ Precipitate (boundary and/or network)
- ● Multi-Phase
- ▲ Incipient Melting
- ■ Melted
- —— Equiduric Lines
- ▬▬ Boundary of Solid Solution

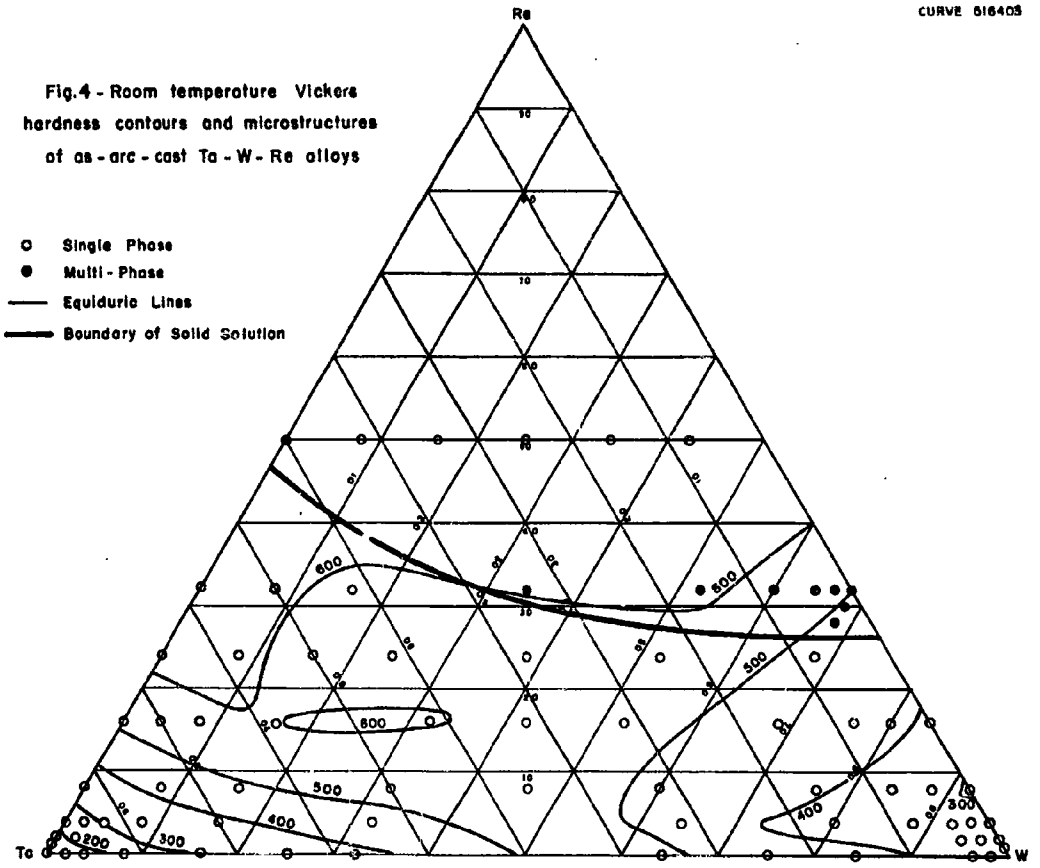

Fig.4 - Room temperature Vickers hardness contours and microstructures of as-arc-cast Ta-W-Re alloys

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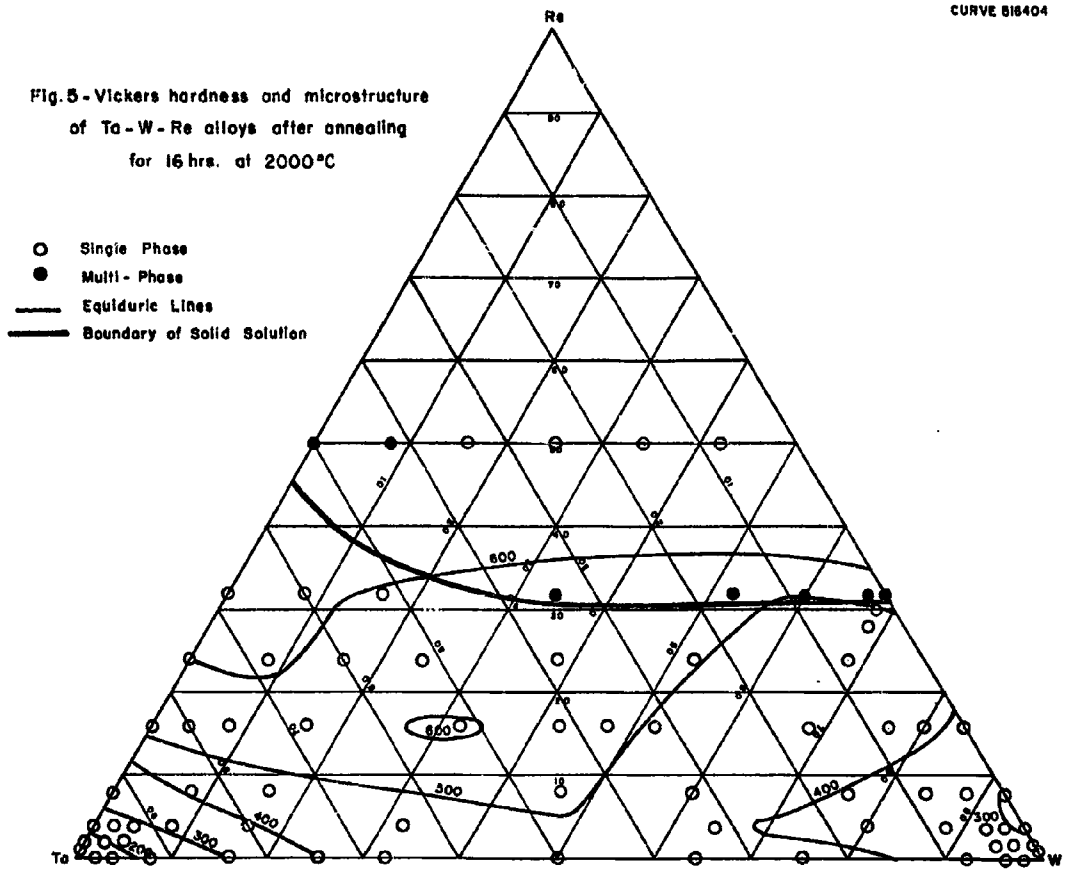

Fig. 5 - Vickers hardness and microstructure of Ta - W - Re alloys after annealing for 16 hrs. at 2000°C

O Single Phase
● Multi - Phase
Equiduric Lines
Boundary of Solid Solution

(2) Ta-W-Hf Annealed 16 Hours at 2000°C, Fig. 3

Two significant differences exist between the as-cast and the as-annealed alloys. A second phase appears in the Ta-rich Ta-W-Hf alloys with Hf content of 2% or more. The nature of this second phase has not been satisfactorily determined. At the same time, throughout most of the Ta-rich corner, an increase in hardness above the as-cast hardness was noted. This could be due to the presence of a very finely dispersed second phase, to contamination during annealing, or to homogenization of the badly cored as arc melted structures. Because of the high strengths found in a later part of the work, the first of these explanations is the most probable. At still higher Hf contents another phase appears. This behavior is believed due to the decomposition of the solid solution into Ta-rich and Hf-rich phases, in agreement with the Ta-Hf phase diagram.

(3) Ta-W-Re, As Arc Melted, Fig. 4

The solubility of Re in Ta and W is quite high, about 25% in W and 45% in Ta. The second phase appearing is either σ phase or χ-phase, depending upon composition, and in either case is very hard. The multiphase regions between the Ta-W solid solution and the complex phases are apparently quite narrow.

Small additions of Re to Ta sharply increase the hardness, although this behavior changes at higher levels of Re. A hardness plateau exists around the 25% Re composition. The initial addition of Re to W sharply decreases the hardness, an anomalous behavior that is still unexplained. The low hardness valley in W-Re is apparently connected to the hardness plateau in Ta-Re and a broad band of unreasonably low hardness extends across the entire diagram.

(4) Ta-W-Re at 2000°C, Fig. 5

The only changes between the as arc melted and the as-annealed system are a general decrease in hardness of 10 to 40 VHN and an increase in the solubility of Re in W to about 30% Re. The hardness anomaly is still present after annealing. The decrease in hardness upon annealing is probably due to reduction of microsegregation or to relief of thermal strains.

Metallographic examination of the Ta-W-Re and Ta-W-Hf systems was carried out using the procedures described in Appendix B. In the Ta-rich corner of the Ta-W-Hf system severe coring was encountered, possibly due to a large liquidus-solidus gap. The coring was largely removed by annealing for 16 hours at 2000°C. Figures 6 and 7 show the microstructures of a Ta-8W-8Hf alloy before and after annealing. The substructure present in this alloy after annealing was found in nearly all of the Ta-base alloys containing more than 2% Hf. This structure is believed to be revealed due to the formation of a hafnium-interstitial compound. At higher Hf levels another phase appeared in the as-annealed microstructures. This phase probably results from the decomposition upon cooling of the b.c.c. solid solution into Hf-rich and Ta-rich phases. The addition of W to these alloys apparently retards this decomposition. Figure 8 shows the microstructure of a Ta-2W-32Hf alloy after annealing at 2000°C and furnace cooling (12 hours to room temperature).

Coring of single phase W base, Hf-containing, alloys was not clearly delineated. A second phase, identified as W_2Hf, was present in as arc melted W alloys containing more than 4% Hf. The addition of up to 32% Ta did not appreciably change the solubility of this phase. Annealing increased the solubility of Hf in W to between 4 and 8%. Figure 9 shows the annealed microstructure of the W-8Ta-8Hf alloy, illustrating the distribution of W_2Hf in a W matrix.

Coring of alloys in the W-Ta-Re system was extensive, but was eliminated by annealing for 16 hours at 2000°C. Figures 10 and 11 represent typical as-cast

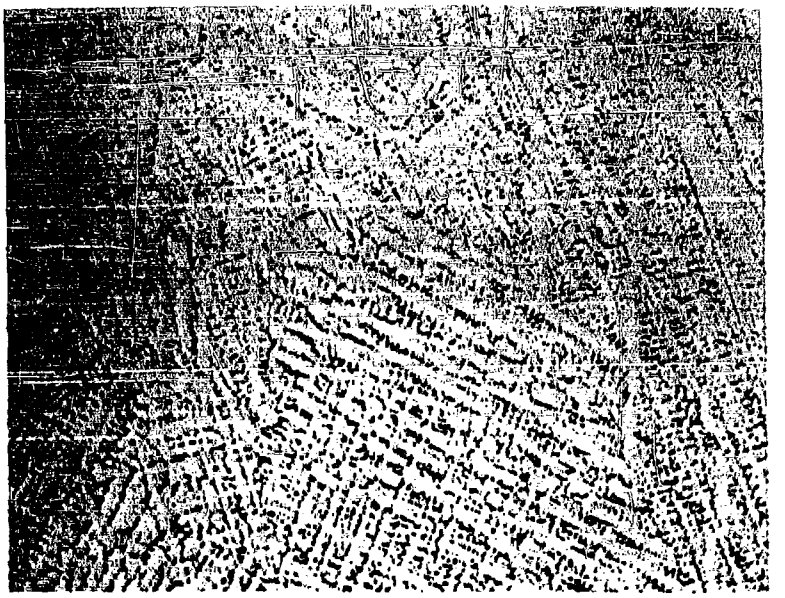

Fig. 6--Microstructure of Ta-8W-8 Hf
As Arc Melted. X100

Fig. 7--Microstructure of Ta-8W-8 Hf
Annealed 16 hours at 2000°C. X200

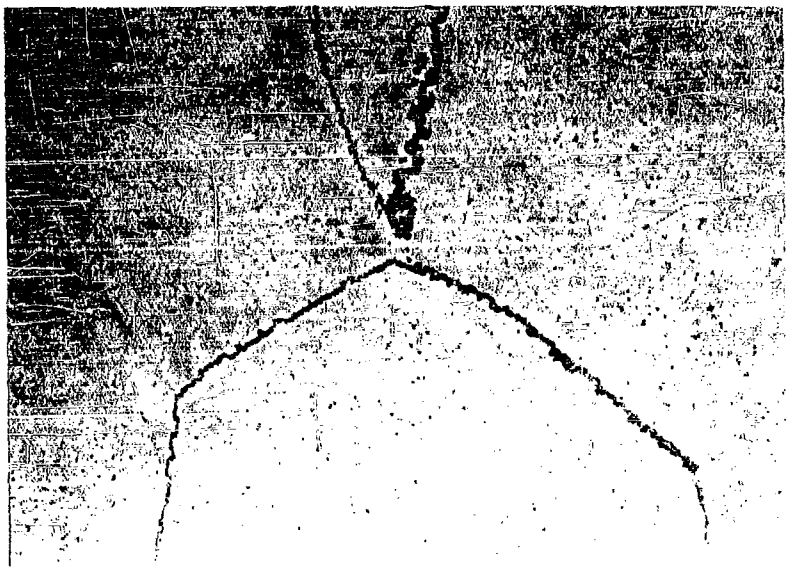

Fig. 8--Microstructure of Ta-2 Hf-32 Hf
Annealed 16 hours at 2000°C. X100

Fig. 9--Microstructure of W-8 Ta-8 Hf
Annealed 16 hours at 2000°C. X200

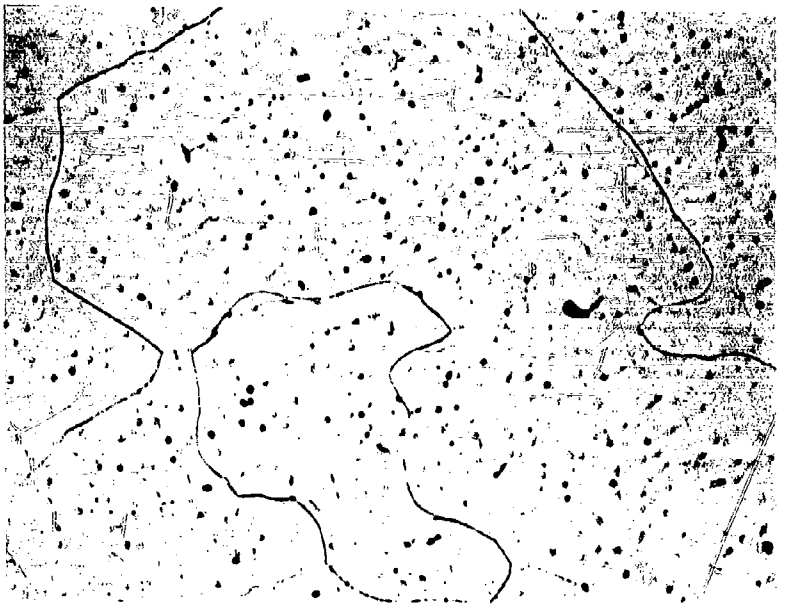

Fig. 10--Microstructure of W-32Ta-8Re
As Arc Melted. X200

Fig. 11--Microstructure of W-32Ta-8Re
Annealed 16 hours at 2000°C. X200

and annealed single phase microstructures. The first excess phase appears between 26% and 46% Re and is either σ or χ, depending upon the alloy content. Figures 12 and 13 illustrate the structure of an alloy (W-32Re-4Ta) which is near the limit of solubility. As indicated by these figures, the solubility of Re in the W-Ta-base solid solution is increased by annealing. Figure 14 shows a multi-phase alloy, 42Ta-8W-50Re, illustrating the fine distribution of phases after annealing.

The data in Table II show hot and cold workability of selected compositions in the Ta-W, Ta-Hf and Ta-W-Hf systems. Binary alloys of Ta-W showed excellent cold fabricability to 8% W, as illustrated in Figure 15. Binary alloys of Ta-Hf showed excellent cold workability only up to 2% Hf addition, as shown in Figure 16. No attempt was made to cold work the Ta-W-Hf alloys. Results of hot working these alloys are shown in Figure 17, indicating good workability to the 4W - 4Hf level. Hot workability of Ta-16W and Ta-32W alloys was good, as was Ta-5Hf, Ta-8Hf and Ta-10Hf. The Ta-16Hf was only fair but the Ta-32Hf was good. Several of these specimens are shown in Figure 18.

In addition to the previous evaluation tests discussed, a number of oxidation tests were conducted on alloys in the Ta-W-Hf and Ta-W-Re ternary systems. The procedure used was to expose measured and weighed rectangular (0.2 x 0.2 x 0.5 inches) specimens for one hour in a tube furnace heated to 1200°C, which contained an undried flowing air atmosphere. Samples were placed in shallow alumina boats. After exposure the specimens were re-weighed and the weight gain in $mg/cm^2/hr.$ determined. The scale was visually examined and described qualitatively in terms of thickness, appearance and adherence. The results of this investigation are listed in Table III. A photograph of several of these oxidation specimens is shown in Figure 19.

The structures of the scales formed on a number of selected binary and ternary Ta-Hf and Ta-W-Hf alloys, during exposure to undried flowing air for one hour at 1200°C, were examined by metallographic techniques. The purpose of this examination was to determine if the alloys having better scaling resistance possessed any peculiarities in structure.

Fig. 12--Microstructure of W-32Re-4Ta
As Arc Melted. X100

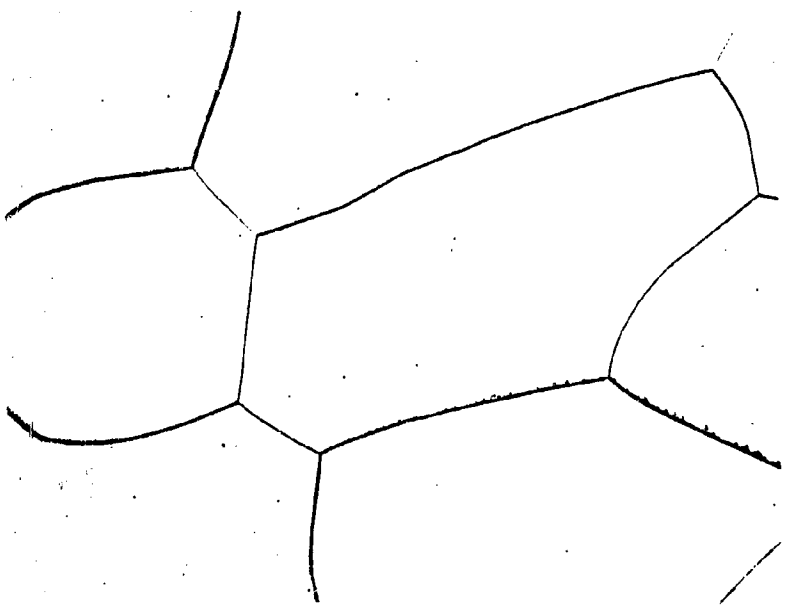

Fig. 13--Microstructure of W-32Re-4Ta
Annealed 16 hours at 2000°C. X200

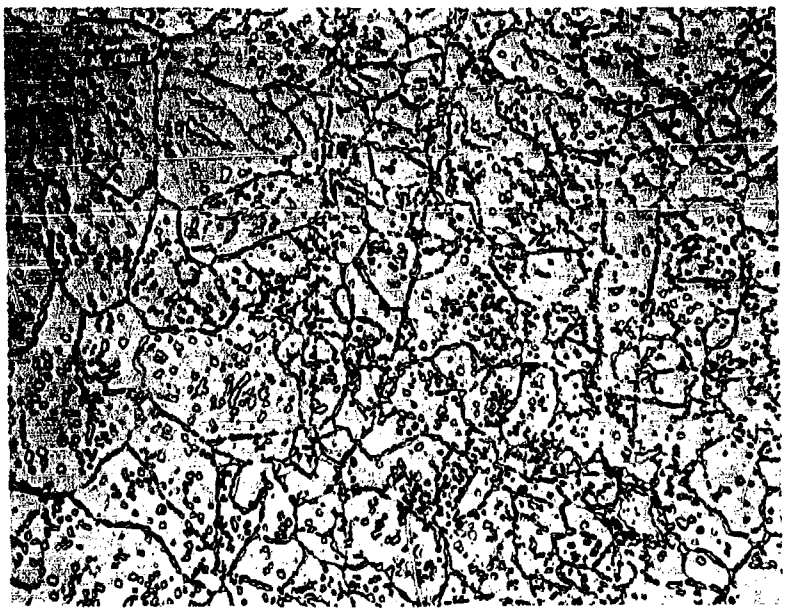

Fig. 14--Microstructure of 42Ta-8W-50Re
Annealed 16 hours at 2000°C. X500

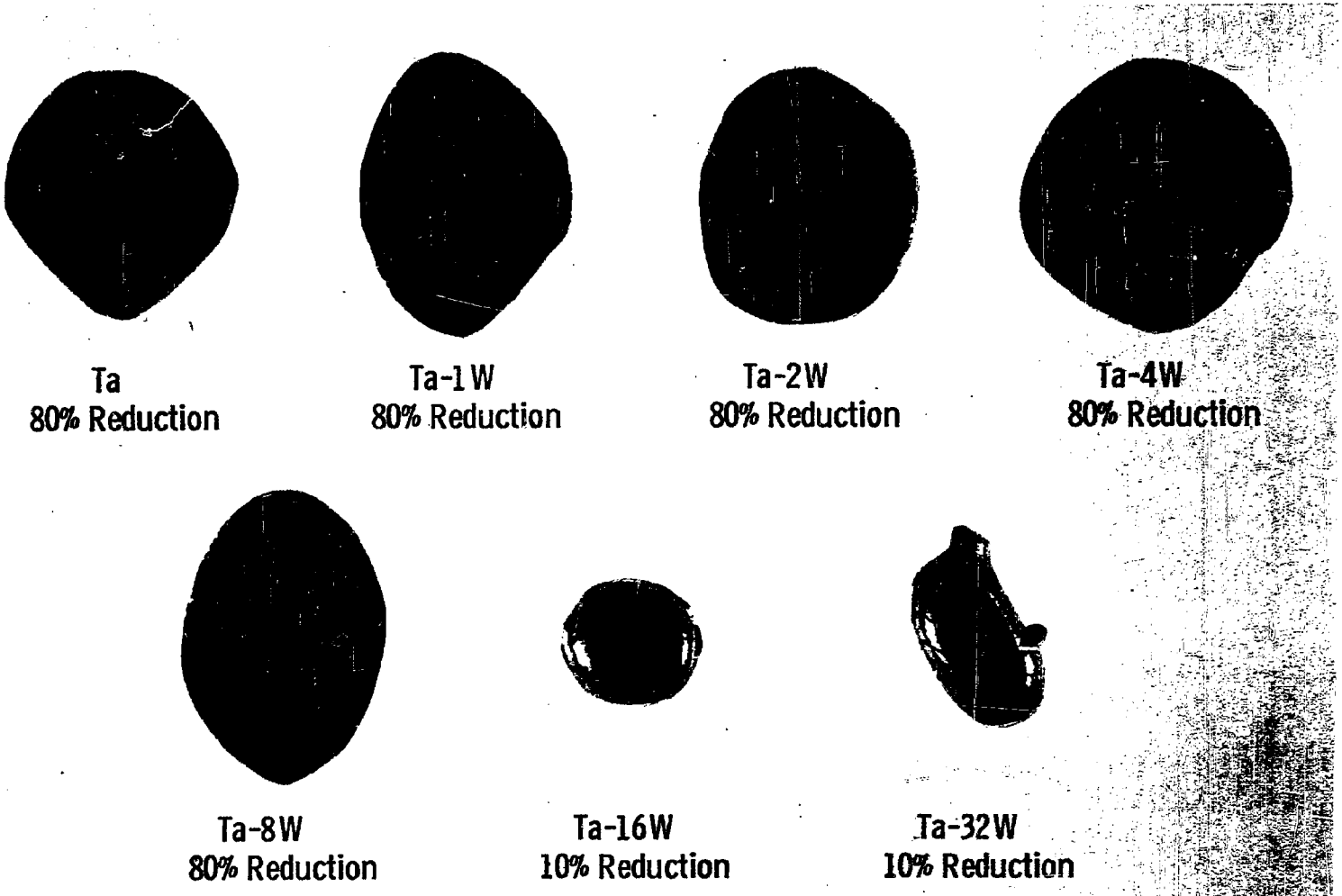

Fig. 15--Tantalum - Tungsten alloy buttons after cold rolling.
Initial condition as cast.

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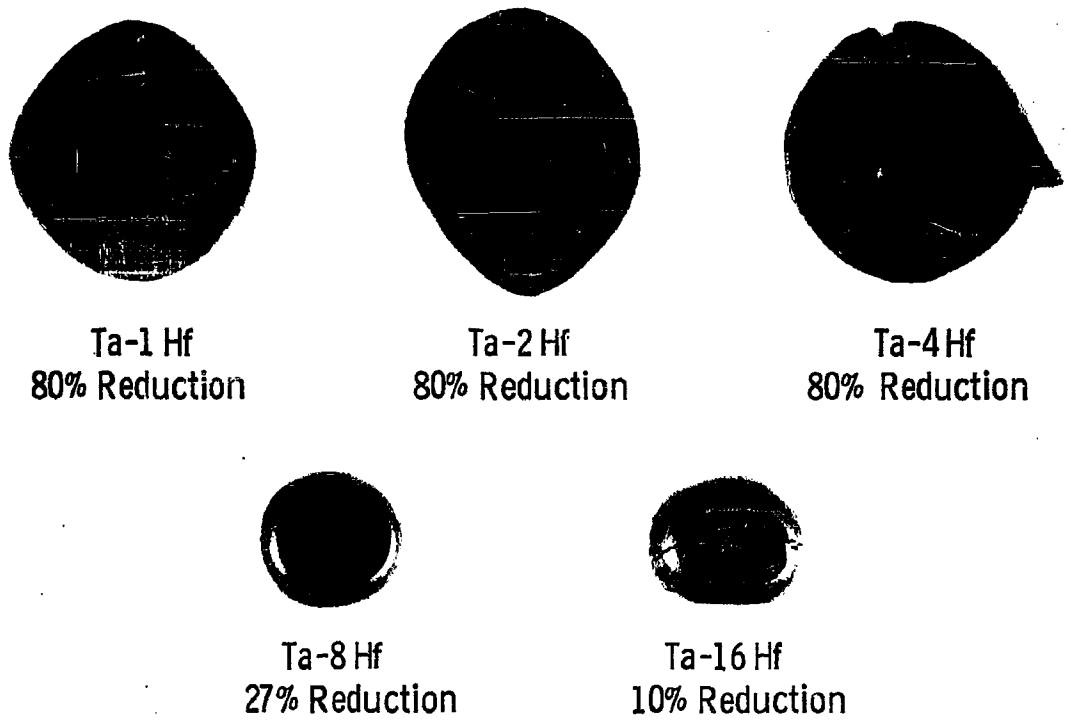

Fig. 16--Tantalum - Hafnium alloy buttons after cold rolling. Initial condition as cast.

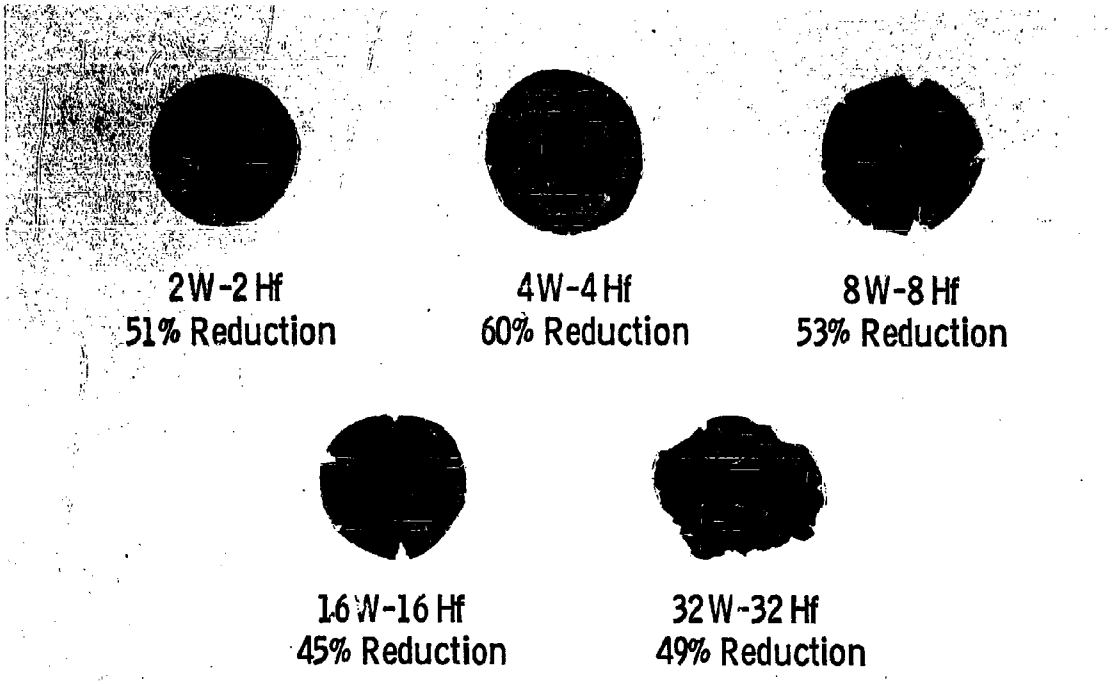

Fig. 17--Tantalum base alloy buttons after hammer forging at 1200°C initial condition as cast.

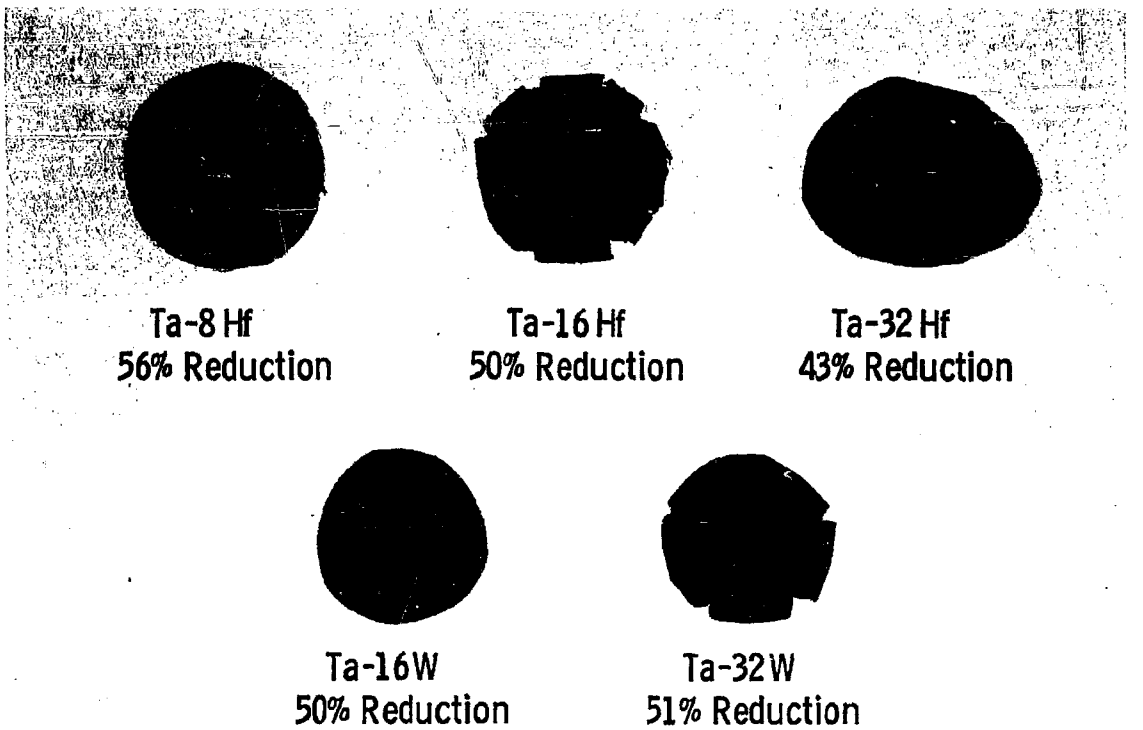

Fig. 18--Tantalum base alloy buttons after hammer forging at 1200°C. Initial condition as cast.

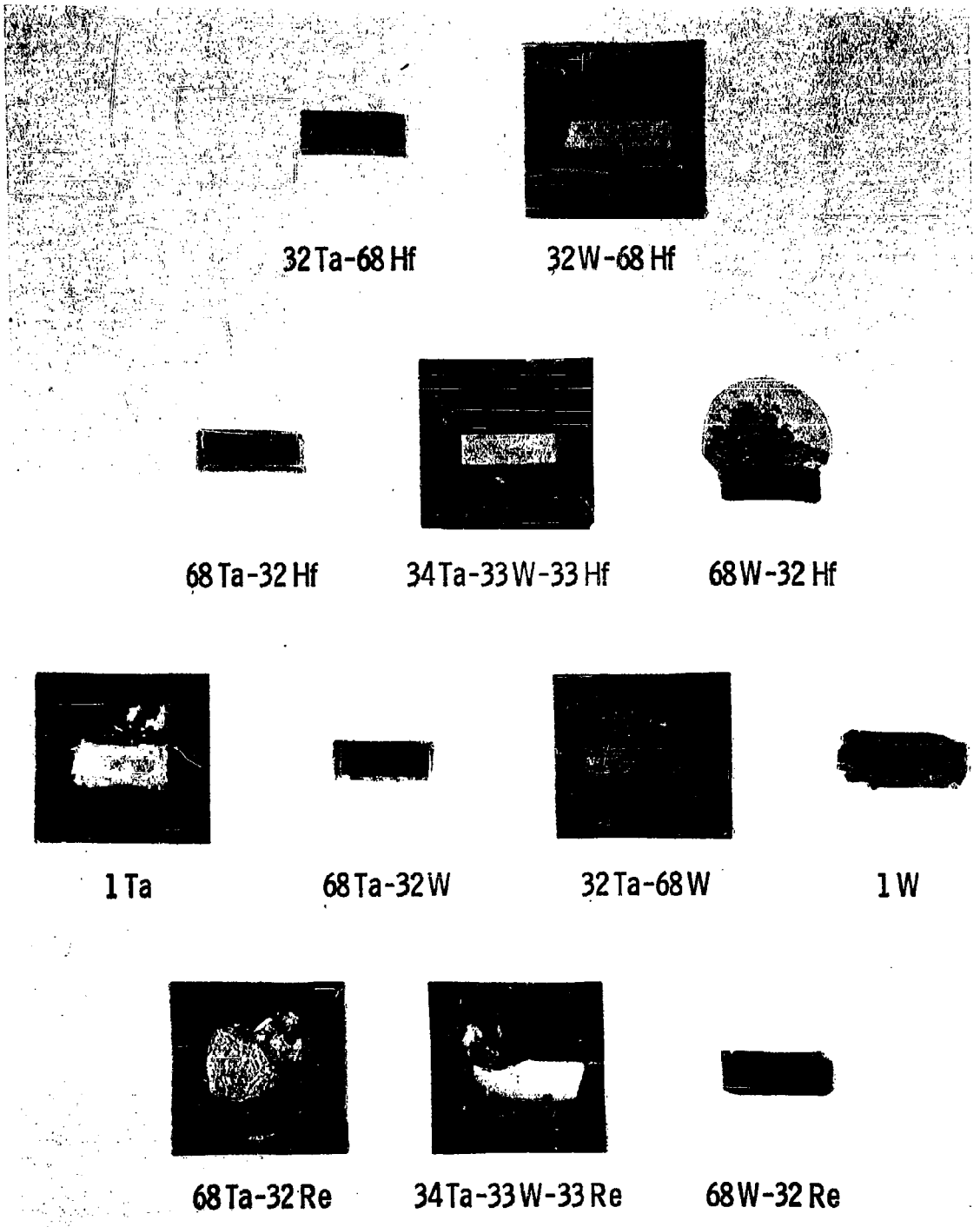

Fig. 19--Scaling of alloys in the Ta-W-Hf and Ta-W-Re systems after 1 hour at 1200°C in undried air.

68Ta-32Hf - Wt. gain 29 mg/cm^2/hr. Four scale layer. Outer layer thin, somewhat porous, dark colored; next layer thin, compact, and dark gray in color; third layer was of a thickness of about twice either of the outer two layers, compact, light gray in color; the thickness of the fourth layer was comparable to that of the third layer, was compact, very light gray color. Thin subscale layer. All layers adherent.

32Ta-68Hf - Wt. gain 10 mg/cm^2/hr. Outer scale thin, compact, gray colored. Subscale layer 1.5 times as thick as outer scale. Beneath the subscale layer there appeared a zone consisting of a Widmanstätten precipitate in the matrix. The depth of this zone was considerably greater at grain boundaries. It appears that the diffusion of oxygen (and perhaps nitrogen) into the alloy has produced a structure with a greater quantity of the h.c.p. phase than was present in the original composition.

34Ta-33W-33Hf - Wt. gain 18 mg/cm^2/hr. Thin, compact, gray outer scale. Subscale layer slightly thicker than outer scale layer. Good adherence of scale layer.

92Ta-4W-4Hf - Wt. gain 101 mg/cm^2/hr. Thick outer scale, compact, light gray in color. Thin subscale layer.

84Ta-8W-8Hf - Wt. gain 24 mg/cm^2/hr. Two oxide layers. Outer layer medium thickness, compact, dark gray colored. Inner layer medium thickness, compact, light gray in color. Thin subscale layer. Good adherence of all scale layers.

76Ta-8W-16Hf - Wt. gain 32 mg/cm^2/hr. Two scale layer. Thick, compact, gray outer scale. Inner scale 1/3 thickness of outer scale, compact, light gray in color. Tendency to spall at interface between these two layers. Very thin subscale layer.

69Ta-26W-5Hf - Wt. gain 64 mg/cm^2/hr. Outer scale medium thickness, dark gray, very porous. Thin subscale layer.

48Ta-48W-4Hf - Wt. gain 26 mg/cm^2/hr. Outer portion of scale had spalled off during the test and while cooling from the test temperature. Remaining scale was thin, slightly porous, dark gray colored. Tendency to spall at interface with alloy. Thin subscale layer.

36Ta-60W-4Hf - Wt. gain 7.5 mg/cm^2/hr. (Low value, probably due to the volatilization of tungsten oxide during test). Thin, slightly porous, dark colored outer scale layer. Thin subscale layer. Scale layer adherent. Several tendencies can be noted from these observations. From the features of the 32Ta-68Hf and 34Ta-33W-33Hf alloys, it appears that a thicker subscale layer contributes to scaling resistance on the basis of weight gain. The increasing addition of Hf seems to enhance scaling resistance by formation of thicker subscale layers and the creation of an additional number of scale layers.

The weight gain values of 77 and 105 mg/cm^2/hr reported for pure W and pure Ta, respectively, are considered excessive for practical use of these materials in an oxidizing environment. These pure metals are known to have high oxidation rates at elevated temperatures. However, the best alloys tested had weight gains of 7.5 - 20 mg/cm^2/hr. This was only a 5 to 10 fold improvement over the pure metals. Although the oxidation rate has been retarded somewhat by alloying, all of these alloys have inferior resistance at 1200°C and could not be considered for use at this temperature in oxidizing atmospheres without the use of protective coatings. Because of these discouraging results on oxidation testing, the effort to obtain extensive oxidation data during the balance of the program was greatly curtailed.

B. PHASE III - SECONDARY SCREENING STUDIES - 20 gram buttons of desired compositions were prepared in the same manner as in Phase I. No master alloys were used, the alloy additions being compacted into the base material as uniformly as possible before melting. Chemical analyses on melted tantalum alloy buttons confirmed that recovery of all additions but chromium was good during the melting operation. Chromium loss was severe as was expected on the basis of its high vapor pressure at the melting point of tantalum. Analyses of tungsten alloy buttons revealed the loss of significant quantities of vanadium and small amounts of rhenium and niobium. Comparison of nominal and actual analyses are shown in Table IV for the addition elements Mo, Cr, Zr, Ti and V in tantalum. Table V illustrates the same thing for the elements

TABLE IV

COMPARISON OF NOMINAL AND ANALYZED COMPOSITIONS IN PHASE III TANTALUM-BASE ALLOYS

Addition Element	Expected Composition Wt. %	Analyzed Composition Wt. %	% Recovery
Mo	1.07	1.09	102
	2.16	3.13	145
	4.41	4.43	101
Cr	0.58	0.02	3
	1.18	0.09	8
	2.44	0.20	8
Zr	1.02	1.26	124
	2.06	3.06	148
	4.20	4.10	98
	8.8	8.43	96
Ti	0.54	0.89	165
	1.10	1.50	136
	2.25	2.12	94
	4.80	2.59	54
V	0.57	0.51	90
	1.16	0.89	77
	2.39	1.99	83
	5.10	6.20	121

TABLE V

COMPARISON OF NOMINAL AND ANALYZED COMPOSITIONS IN PHASE III TUNGSTEN-BASE TERNARY ALLOYS

Addition Element	Expected Composition Wt. %	Analyzed Composition Wt. %	% Recovery
Re	2.04	1.86	91
Nb	1.00	1.03	103
Re	2.06	1.89	92
Nb	2.06	1.50	73
Re	4.09	3.97	97
Nb	1.01	0.96	95
Re	2.05	1.99	97
V	0.56	0.16	29
Re	4.10	3.94	96
V	0.56	0.26	47

Re, Cb and V in tungsten ternary alloys. There appears to be considerable segregation present in the cast alloys, as evidenced by some of the recovery values in excess of 100%. Similarly, some of the lower recovery values might not be indicative of true metal loss, since samples might have been selected from areas deficient in the added element.

Ta-Mo. The recovery of molybdenum in the button melt was satisfactory.

Ta-Zr. Zirconium recovery was quite good, and the difference between the nominal and analyzed composition is believed to be caused by segregation.

Ta-Ti. Titanium behaves like zirconium as far as recovery is concerned, even though "smoke" is formed above the molten button.

Ta-V. The recovery of vanadium in the Ta-base alloy buttons seems rather consistent. The problem of analyzing the alloy addition recovery in the 20 gram buttons was complicated by the possible inhomogeneity of the button. Even though care was taken during the melting procedure to produce homogeneity by melting each button a minimum of four times, the possibility of segregation still existed.

Information on analytical chemistry techniques employed during the course of this project are contained in Appendix C of this report. The procedures used for evaluation of Phase III alloys paralleled those employed in Phase I. These included hardness, microstructure, workability and oxidation of 20 gram specimens buttons in the cast and/or heat treated conditions. The results are summarized in Tables VI-IX and in Figures 20-21. All alloy compositions are reported in weight per cent and annealing treatments were 16 hours at 2000°C unless otherwise specified.

Table VI contains data on the cast and annealed Vickers hardnesses of a number of binary and ternary tantalum and tungsten alloys. In this series, Zr and Ti have been substituted generally for Hf while Mo, Cr and V have replaced Re, W and Ta in the original Phase I Ta-W-Hf and Ta-W-Re compositions. The hardness of Ta at room temperature is increased by the binary addition of Re, V, Mo, Zr, W, Hf and Ti, listed in order of decreasing effectiveness (Fig. 20).

TABLE VI. STRUCTURE AND HARDNESS OF PHASE III ALLOYS

Composition	Structure[1] and Hardness (VHN) Cast	2000°C Homog.
Ta-1.1Mo	S.P.-161	S.P.-126
Ta-2.2Mo	S.P.-207	S.P.-170
Ta-4.4Mo	S.P.-249	S.P.-210
Ta-9.2Mo	S.P.-319	S.P.-314
Ta-20Mo	S.P.-424	S.P.-386
Ta-48.5Mo	S.P.-459	S.P.-391
Ta-0.02Cr	S.P.-115	S.P.-86
Ta-0.09Cr	S.P.-120	S.P.-83
Ta-0.20Cr	S.P.-144	S.P.-111
Ta-34Cr	S.P.-806	--
Ta-1.0Zr	T.P.-167	T.P.-149
Ta-2.1Zr	T.P.-170	T.P.-207
Ta-4.2Zr	T.P.-204	T.P.-267
Ta-8.8Zr	T.P.-305	T.P.-558
Ta-19.2Zr	T.P.-366	T.P.-319
Ta-47.3Zr	T.P.-390	T.P.-Melted
Ta-2Zr	T.P.-190	T.P.-207
Ta-4Zr	T.P.-198	T.P.-261
Ta-8Zr	T.P.-285	T.P.-404
Ta-10Zr	T.P.-332	T.P.-313
Ta-16Zr	T.P.-331	T.P.-284
Ta-30Zr	T.P.-385	T.P.-Melted
Ta-0.5Ti	S.P.-112	- 106
Ta-1.1Ti	S.P.-110	- 112
Ta-2.3Ti	S.P.-132	- 140
Ta-4.8Ti	S.P.-167	- -
Ta-11.1Ti	S.P.-182	- -
Ta-32.0Ti	S.P.-168	T.P.-284
Ta-0.6V	S.P.-136	S.P.-118
Ta-1.2V	S.P.-150	S.P.-136
Ta-2.4V	S.P.-201	S.P.-190
Ta-5.1V	S.P.-301	S.P.-288
Ta-11.7V	S.P.-413	S.P.-386
Ta-33.4V	S.P.-456	S.P.-405
W-2Zr	S.P.-398	T.P.-393
W-4.1Zr	T.P.-514	T.P.-480
W-7.8Zr	S.P.-490	T.P.-483
W-18.9Zr	T.P.-665	T.P.-569
W-1Ti	S.P.-366	S.P.-361
W-2.3Ti	S.P.-393	S.P.-362
W-4.2Ti	S.P.-397	S.P.-378
W-10.9Ti	S.P.-362	S.P.-384
W-1V	S.P.-356	S.P.-368
W-2.3V	S.P.-364	S.P.-368
W-4.5V	S.P.-351	S.P.-355
W-11.5V	S.P.-409	S.P.-387
Ta-1Mo-1V	S.P.-172	S.P.-166
Ta-2Mo-2V	S.P.-224	S.P.-226
Ta-4Mo-4V	S.P.-302	S.P.-316
Ta-1Mo-1Zr	S.P.-187	S.P.-187
Ta-2Mo-2Zr	S.P.-286	- 331
Ta-4Mo-4Zr	S.P.-313	- 351
Ta-8Mo-8Zr	T.P.-408	T.P.-442
Ta-16Mo-16Zr	T.P.-466	- Melted
Ta-32Mo-32Zr	T.P.-493	- Melted
Ta-1Mo-1Hf	S.P.-166	S.P.-152
Ta-2Mo-2Hf	S.P.-212	- 238
Ta-4Mo-4Hf	- 281	- 313
Ta-8Mo-8Hf	- 383	- 410
Ta-16Mo-16Hf	S.P.-488	- 470
Ta-32Mo-32Hf	- 579	T.P.-538
Ta-2W-1Zr	T.P.-178	T.P.-168
Ta-2W-1Zr	S.P.-185	S.P.-176
Ta-2W-2Zr	S.P.-193	- -
Ta-2W-4Zr	T.P.-228	T.P.-270
Ta-4W-4Zr	T.P.-262	T.P.-301
Ta-8W-4Zr	T.P.-316	T.P.-344
Ta-8W-8Zr	T.P.-376	- -
Ta-8W-2Zr	T.P.-275	S.P.-270
Ta-16W-16Zr	T.P.-429	T.P.-359
Ta-38W-19Zr	T.P.-488	- -
Ta-49W-2Zr	S.P.-490	T.P.-493
Ta-48W-4Zr	S.P.-523	- -
Ta-46W-9Zr	S.P.-486	- -
Ta-19W-19Zr	S.P.-436	- -

TABLE VI. (Cont'd)

Composition	Structure[1] and Hardness (VHN) Cast	2000°C Homog.
Ta-2W-0.5Ti	S.P.-162	- -
Ta-4W-1Ti	S.P.-163	- -
Ta-42W-11Ti	S.P.-451	- -
Ta-50W-1Ti	S.P.-472	- 465
Ta-49W-2Ti	S.P.-486	- -
Ta-48W-5Ti	S.P.-481	- -
Ta-21W-11Ti	S.P.-314	- 425
Ta-2W-0.6V	S.P.-155	S.P.-146
Ta-2W-1V	S.P.-171	S.P.-166
Ta-2W-2V	S.P.-197	S.P.-183
Ta-4W-4V	S.P.-280	S.P.-268
Ta-8W-8V	S.P.-388	S.P.-375
Ta-16W-16V	S.P.-440	- -
Ta-32W-32V	S.P.-500	- -
Ta-42W-12V	S.P.-566	S.P.-488
Ta-50W-1V	S.P.-477	S.P.-490
Ta-49W-2V	S.P.-484	S.P.-485
Ta-48W-5V	S.P.-528	S.P.-525
Ta-21W-12V	S.P.-314	S.P.-474
W-2Re-0.6V	S.P.-328	S.P.-343
W-2Re-1V	S.P.-330	S.P.-344
W-4Re-0.6V	S.P.-302	S.P.-310
W-8Re-2V	S.P.-324	S.P.-307

Composition	Structure[1] and Hardness (VHN) Cast	2000°C Homog.
W-2Re-1Cb	S.P.-336	S.P.-354
W-2Re-2Cb	S.P.-346	S.P.-365
W-2Re-2Cb	S.P.-353	S.P.-350
W-4Re-1Cb	S.P.-307	S.P.-312
W-4.1Re-1Cb	S.P.-303	S P.-302
W-4Re-2Cb	S.P.-358	S.P.-335
W-4.1Re-2Cb	S.P.-335	S.P.-324
W-4.2Re-4.1Cb	S.P.-371	S.P.-365
W-4.1Re-8.1Cb	S.P.-381	S.P.-353
W-8Re-4Cb	S.P.-351	S.P.-331

(1) S.P. - Single Phase

T.P. - Two Phase

TABLE VII

WORKABILITY OF PHASE III TANTALUM BASE ALLOYS

All Alloys Hammer Forged (One Blow) at 1200°C

Composition	% Reduction	Remarks
Ta-0.6V	68	Very Good; No Edge Cracks
Ta-1.2V	70	" " " " "
Ta-2.4V	64	" " " " "
Ta-5.1V	65	" " " " "
Ta-11.7V	49	Fair; Edge Cracks
Ta-1Zr	66	Very Good; No Edge Cracks
Ta-2.1Zr	59	Good; Minor Edge Cracks
Ta-4.2Zr	49	Fair; Edge Cracks
Ta-8.8Zr	58	Good; Minor Edge Cracks
Ta-19.2Zr	52	" " " "
Ta-1V-1Mo	66	Very Good; No Edge Cracks
Ta-2V-2Mo	62	" " " " "
Ta-4V-4Mo	46	Fair; Edge Cracks
Ta-8V-8Mo	38	Poor; Deep Edge Cracks
Ta-16V-16Mo	27	" " " "
Ta-32V-32Mo	40	" " " "
Ta-1Zr-1Mo	64	Good; Minor Edge Cracks
Ta-2Zr-2Mo	57	" " " "
Ta-4Zr-4Mo	56	Poor; Deep Edge Cracks
Ta-8Zr-8Mo	57	" " " "
Ta-16Zr-16Mo	52	" " " "
Ta-32Zr-32Mo	32	" " " "
Ta-1Hf-1Mo	59	Very Good; No Edge Cracks
Ta-2Hf-2Mo	58	" " " " "
Ta-4Hf-4Mo	46	Good; Minor Edge Cracks
Ta-8Hf-8Mo	52	Poor; Deep Edge Cracks
Ta-16Hf-16Mo	39	" " " "
Ta-32Hf-32Mo	-	Shattered

TABLE VIII

LIMIT OF WORKABILITY FOR TANTALUM ALLOYS

Alloys Upset Forged at 1200°C

Workable with Minor Edge Cracks (<5% of Diameter)		Workable with Medium Edge Cracks	
Composition	VHN	Composition	Hardness
Ta-5.1V	301	Ta-11.7V	413
Ta-19Zr	366	---	---
Ta-32Hf	366	---	---
Ta-32W	391	---	---
Ta-2V-2Mo	224	Ta-4V-4Mo	302
Ta-2Zr-2Mo	286	Ta-4Zr-4Mo	313
Ta-4Hf-4Mo	281	Ta-8Hf-8Mo	383
Ta-4V-4W	280	Ta-8V-8W	388
Ta-2Zr-2W	193	Ta-4Zr-4W	262
Ta-4Hf-4W	212	Ta-8Hf-8W	289

TABLE IX

OXIDATION RESISTANCE OF PHASE III ALLOYS(1)

Composition (%)	Weight Gain mg/cm²/hr.	Comments on Scale
Ta-0.6V	118	Thick, Non-adherent Gold Outer Scale. Black Subscale.
Ta-1.2V	116	Thick, Non-adherent Gold Outer Scale. Black Subscale.
Ta-2.4V	106	Thick, Non-adherent Gold Outer Scale. Black Subscale.
Ta-5.1V	100	Oxide Melted.
Ta-11.7V	67	Thin, Non-adherent Brown Outer Scale. Black Subscale.
Ta-1Zr	120	Fluffy, Adherent Yellow Outer Scale. Black Subscale.
Ta-2.1Zr	120	Fluffy, Adherent Yellow Outer Scale. Black Subscale.
Ta-4.2Zr	68	Thick, Non-adherent Yellow Outer Scale. Black Subscale.
Ta-8.7Zr	---	Thin, Adherent Yellow Outer Scale. Black Subscale.
Ta-19.2Zr	42	Thin, Adherent Yellow Outer Scale. Black Subscale.
Ta-2W-1V	---	Fluffy, Adherent Brown Outer Scale. Gray Subscale.
Ta-2W-2V	78	Non-adherent Dark Brown Outer Scale. Black Subscale.
Ta-4W-4V	58	Non-adherent Dark Brown Outer Scale. Black Subscale.
Ta-8W-8V	---	Oxide Melted.
Ta-16W-16V	---	Oxide Melted.
Ta-32W-32V	---	Oxide Melted.
Ta-2W-1Zr	92	Thick, Adherent Outer Scale. Black Subscale.

(1) Specimens Held 1 Hr. at 1200°C in Flowing Air.

TABLE IX. (Cont'd)

Composition (%)	Weight Gain $mg/cm^2/hr.$	Comments on Scale
Ta-2W-2Zr	88	Thick, Adherent Outer Scale. Black Subscale.
Ta-4W-4Zr	74	Thin, Adherent Outer Scale. Black Subscale.
Ta-8W-8Zr	58	Thin, Adherent Outer Scale. Black Subscale.
Ta-16W-16Zr	65	Thick, Powdery Outer Scale. Black Subscale.
Ta-32W-32Zr	174	Fluffy, Adherent Outer Scale
Ta-1Mo-1V	95	Gold Outer Scale. Black Subscale.
Ta-2Mo-2V	93	Thin, Non-adherent Brown Outer Scale. Black Subscale.
Ta-4Mo-4V	68	Thin, Brown Outer Scale. Black Subscale.
Ta-8Mo-8V	---	Oxide Melted.
Ta-16Mo-16V	---	Oxide Melted.
Ta-32Mo-32V	---	Oxide Melted
Ta-1Mo-1Zr	64	Non-adherent Yellow Outer Scale. Black Subscale.
Ta-2Mo-2Zr	62	Thin, Adherent Yellow Outer Scale. Black Surface.
Ta-4Mo-4Zr	66	Thick, Adherent Yellow Outer Scale. Black Subscale.
Ta-8Mo-8Zr	71	Fluffy, Adherent Yellow Outer Scale. Black Subscale.
Ta-10Mo-10Zr	---	Fluffy, Adherent Yellow Outer Scale. Black Subscale.
Ta-32Mo-32Zr	---	Fluffy, Adherent Yellow Outer Scale. Black Subscale.
Ta-1Mo-1Hf	81	Yellow Outer Scale. Black Subscale.
Ta-2Mo-2Hf	88	Fluffy, Adherent Yellow Outer Scale.
Ta-4Mo-4Hf	89	Thick, Powdery, Non-adherent Outer Scale. Black Subscale.
Ta-8Mo-8Hf	63	Yellow Outer Scale. Black Subscale.
Ta-16Mo-16Hf	---	Completely Oxidized.
Ta-32Mo-32Hf	---	Adherent Gold Outer Scale. Black Subscale.

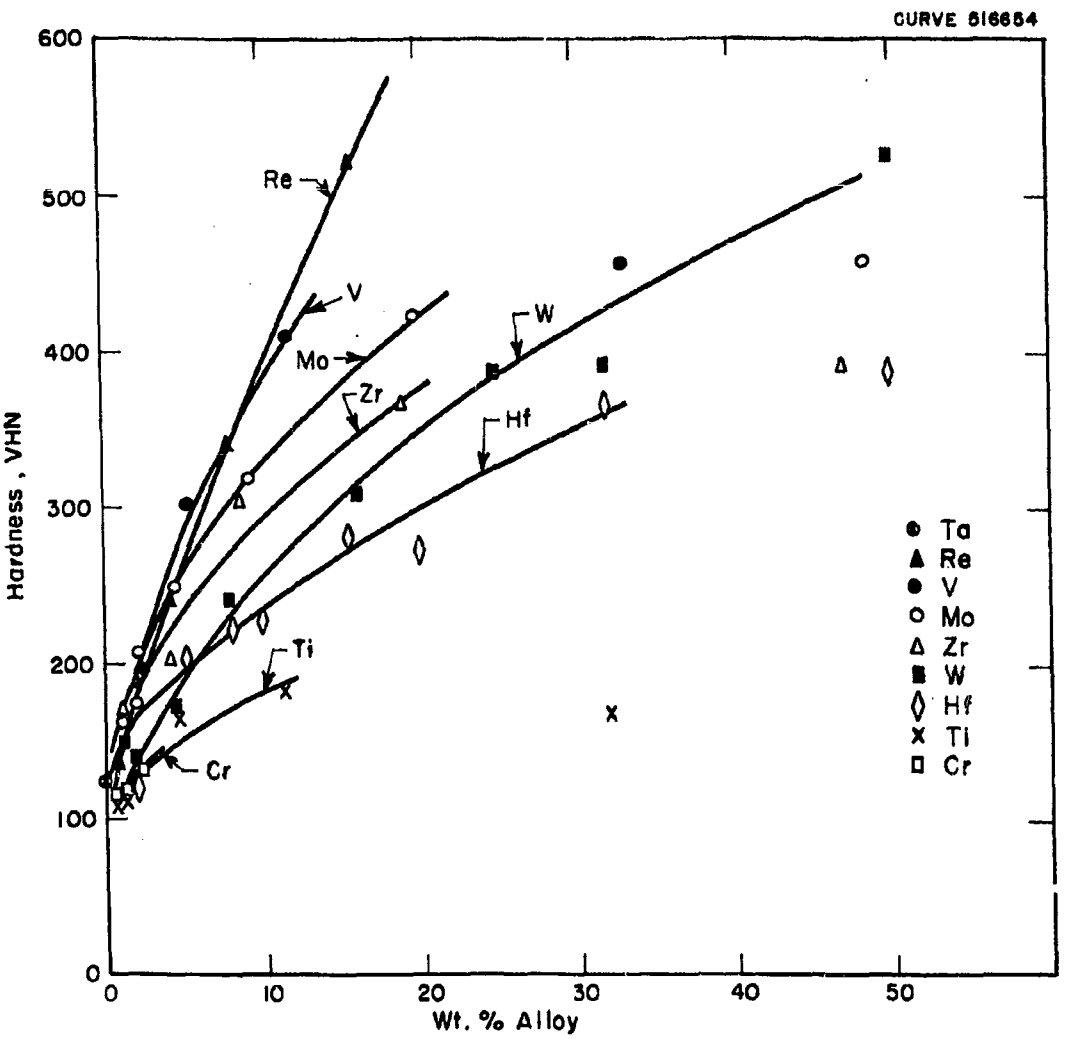

Fig.20—Effect of binary alloying on the room temperature hardness of tantalum base alloys in the as cast condition.

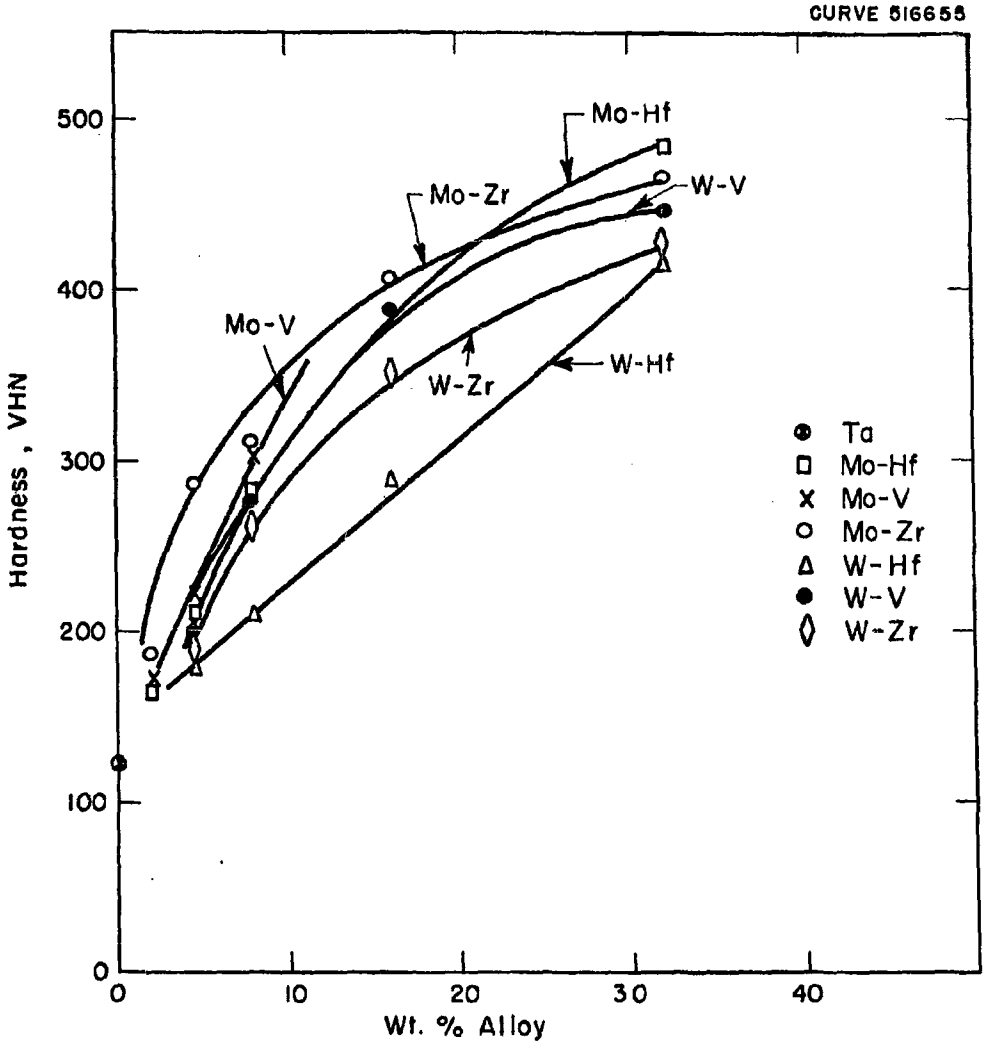

Fig. 21 – Effect of ternary alloying on the room temperature hardness of tantalum base alloys in the as – cast condition. Ternary additions are in 1:1 ratio.

When ternary additions of V and W or V and Mo are made, the resulting change in hardness is intermediate between what would be expected for an equivalent binary addition. However, if Zr or Hf is added simultaneously with Mo or W, the hardness is increased to a value greater than expected from equivalent binary additions of either element.

Figures 22 and 23 show the cored as cast structure and homogeneous annealed structure of a Ta-22Mo alloy. Except for variations in coring, which depends upon alloy content, these photomicrographs are typical of the structures observed in the following systems: Ta-Mo, W-V, Ta-Mo-V, Ta-W-Ti, Ta-W-V, W-Re-V, and W-Re-Nb. Systems containing Cr, Zr, and Hf were found to have limited solid solubility within the ranges investigated.

The high vapor pressure of chromium made it extremely difficult to obtain microstructurally representative alloys. Little chromium could be retained in alloys containing less than 5% Cr. A 12% Cr alloy was multi-phase but inhomogeneous as shown in Fig. 24. The single-phase Ta-33Cr alloy was severely cracked. This alloy probably consists of an intermediate solid solution based upon $TaCr_2$.

Coring was extensive in the W-Zr system. A W-2Zr alloy was heavily cored as cast. The same alloy after annealing contained a second phase, similar in appearance and distribution to W_2Hf in the W-Hf binary or W-Ta-Hf ternary systems (see Fig. 9). Zirconium lowers the melting point of W appreciably. Incipient melting was observed in a W-8Zr alloy after annealing 16 hours at 2000°C.

The Ta-Zr, Ta-W-Zr, and Ta-Mo-Zr systems were microstructurally quite similar. Networks of substructure were present in alloys containing up to 6% Zr after annealing 16 hours at 2000°C. A lamellar grain boundary structure formed during annealing in alloys containing more than 6% Zr. Typical microstructures are shown in Figures 25 through 28. Annealing 16 hours at 2000°C removed all evidence of as cast coring from Ta-Mo-Hf alloys. Annealed alloys contained substructure whose density appeared to increase with Hf content. The as cast and annealed microstructures of the Ta-16Mo-16Hf alloy are shown in Figures 29 and 30 respectively.

Fig. 22--Microstructure of Ta-2.2 Mo
As Arc Melted. X75

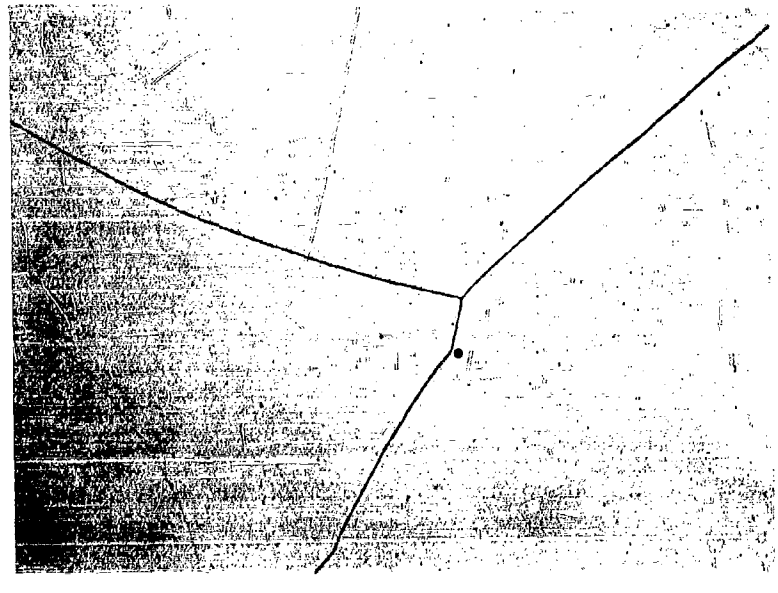

Fig. 23--Microstructure of Ta-2.2 Mo
Annealed 16 hours at 2000°C. X100

Fig. 24--Microstructure of Ta-12 Cr
As Arc Melted. X100

Fig. 25--Microstructure of Ta-4W-2Zr
As Arc Melted. X100

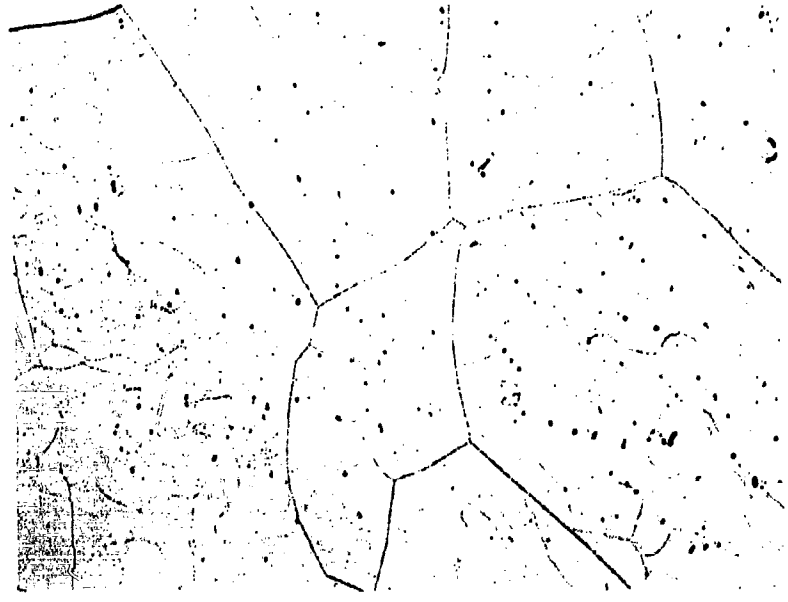

Fig. 26--Microstructure of Ta-4W-2Zr
Annealed 16 hours at 2000°C. X100

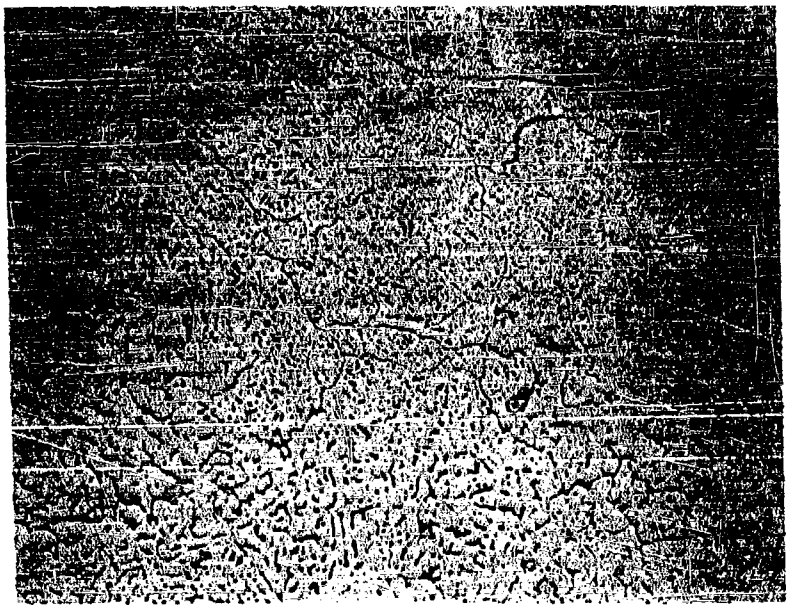

Fig. 27--Microstructure of Ta-8.4Zr
As Arc Melted. X100

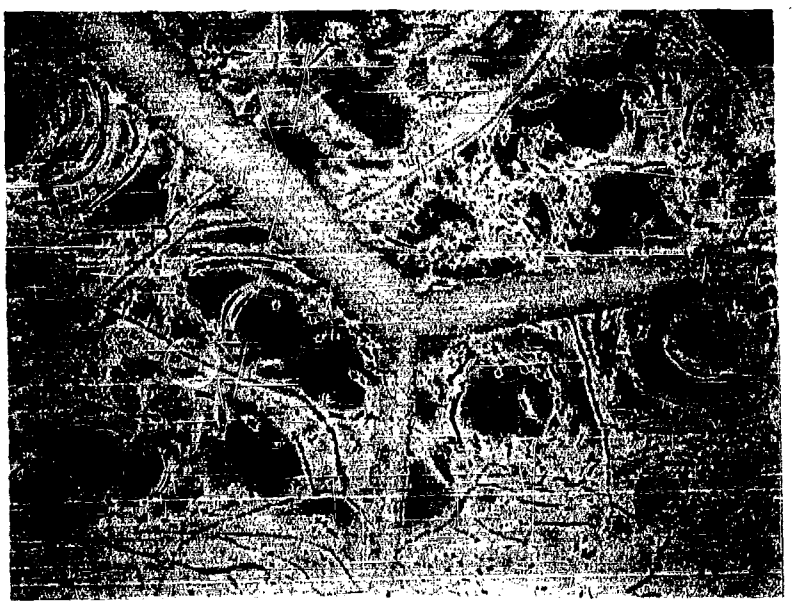

Fig. 28--Microstructure of Ta-8.4Zr
Annealed 16 hours at 2000°C. X100

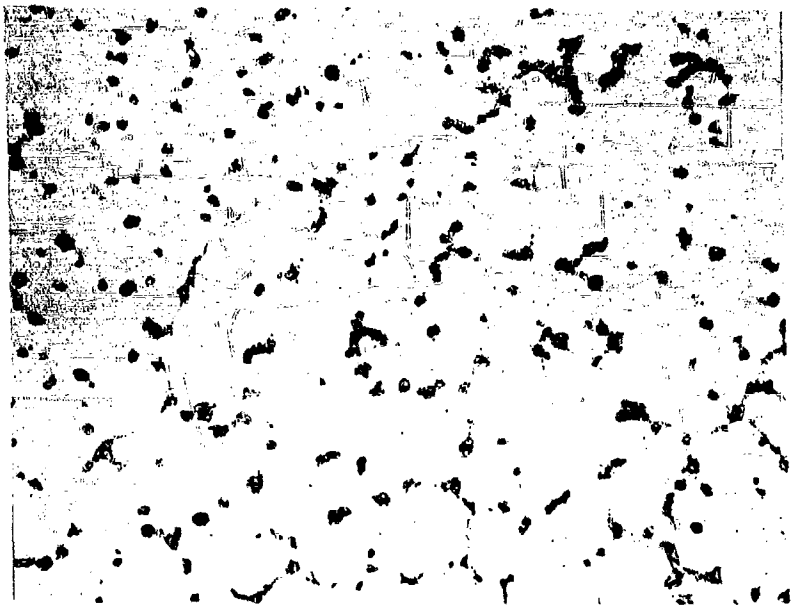

Fig. 29--Microstructure of Ta-16 Mo-16 Hf
As Arc Melted. X500

Fig. 30--Microstructure of Ta-16 Mo-16 Hf
Annealed 16 hours at 2000°C. X500

After annealing for 16 hours at 2000°C, Ta-base alloys containing Zr increased in hardness by a significant amount, similar to the effect noted in Phase I ternary alloys containing Hf. This effect led to the decision to investigate the Ta-Zr binary system in more detail. Metallography, x-ray and chemical analyses were used to obtain detailed information on this system which could then be used to interpret its behavior. A description of this work is included as Appendix D.

Table VII presents the workability information generated by hammer forging tantalum alloy button specimens at 1200°C. Photographs of a number of the specimens after forging are shown in Figures 31-37.

The results were generally encouraging on the two binary systems tested. At 1200°C the alloys containing up to 5% V, or up to 19% Zr, could be upset forged with only minor edge cracking. This is roughly comparable to 32% Hf or 32% W. This workability limit in all four cases occurred when room temperature hardness was in the range of 300-400 VHN. In the three ternary systems investigated, the limit of workability is less. The Ta-2V-2Mo alloy with a 224 VHN was quite workable. The Ta-4V-4Mo with a 302 VHN contained edge cracks when forged at 1200°C. The Ta-Zr-Mo alloys were easily workable at a hardness level of 286 VHN and were difficult at 313 VHN. The Ta-Hf-Mo alloys were workable at 281 VHN and were not fabricable at 383 VHN. The alloys possessing the highest hardness, but still workable at 1200°C, were the binary alloys with 32% W, 32% Hf or 19% Zr. These showed hardnesses of 391, 366, and 366 VHN respectively. No ternary alloy with a hardness greater than 300 VHN was easily workable. Table VIII lists the composition and hardness of the hardest workable alloy in each of the above systems. The criterion used for workability (minor edge cracking) is rather severe; thus it is probable that materials with greater alloy content than shown in Table VIII could be worked satisfactorily.

Oxidation data obtained on the Phase III alloys are shown in Table IX. They are not encouraging and further confirm conclusions drawn in Phase I that the possibilities of developing an oxidation resistant tantalum-base alloy are extremely remote. None of the Phase III alloys had oxidation resistance as good as the Ta-8W-8Hf alloy investigated in Phase I. Zr was the most effective

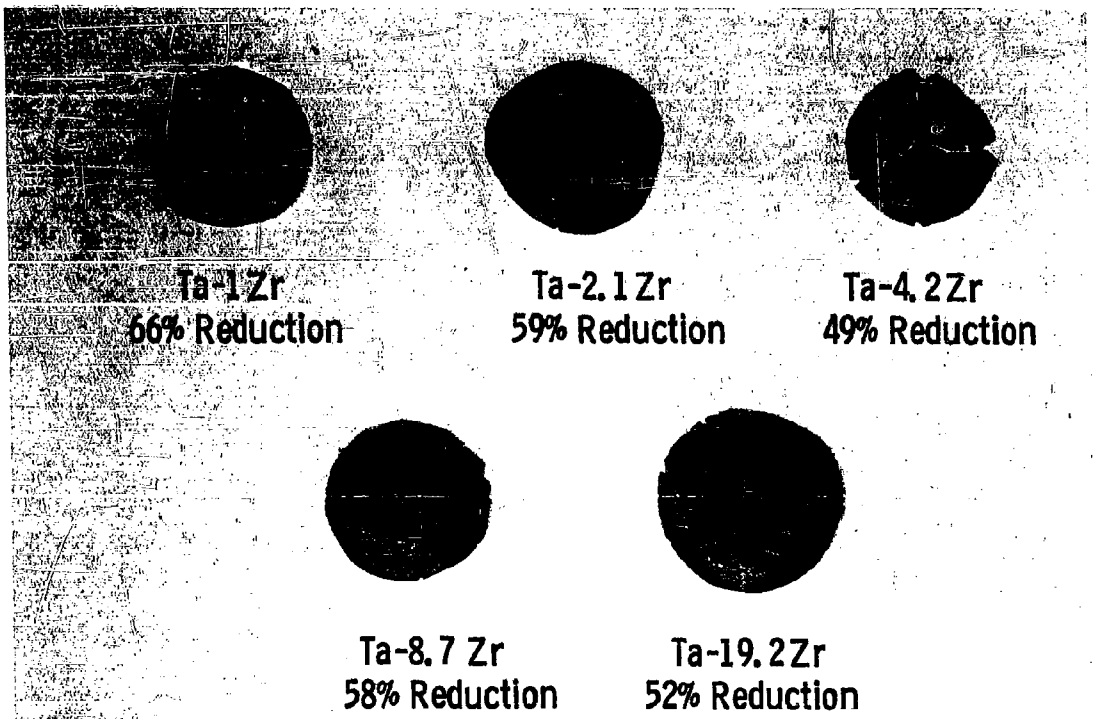

Fig. 31--Arc melted Tantalum - Zirconium buttons after hammer forging at 1200°C.

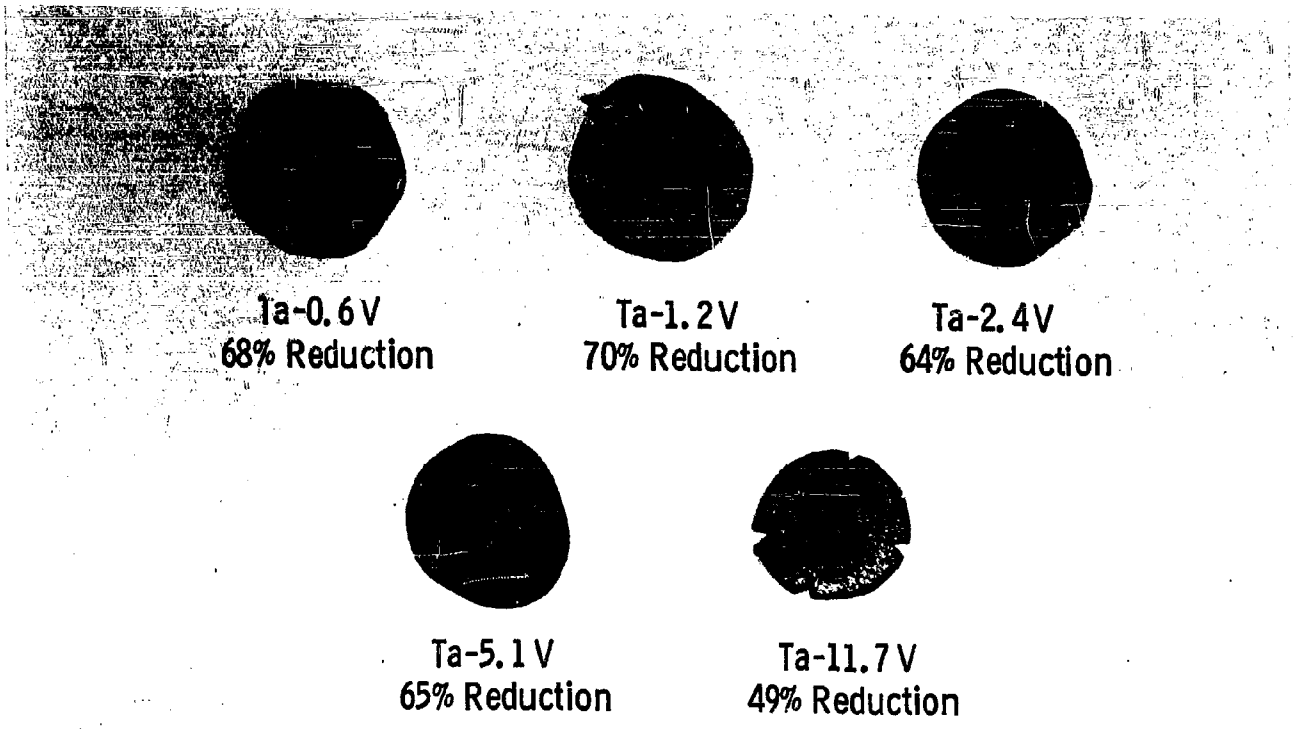

Fig. 32--Arc melted Tantalum - Vanadium buttons after hammer forging at 1200°C.

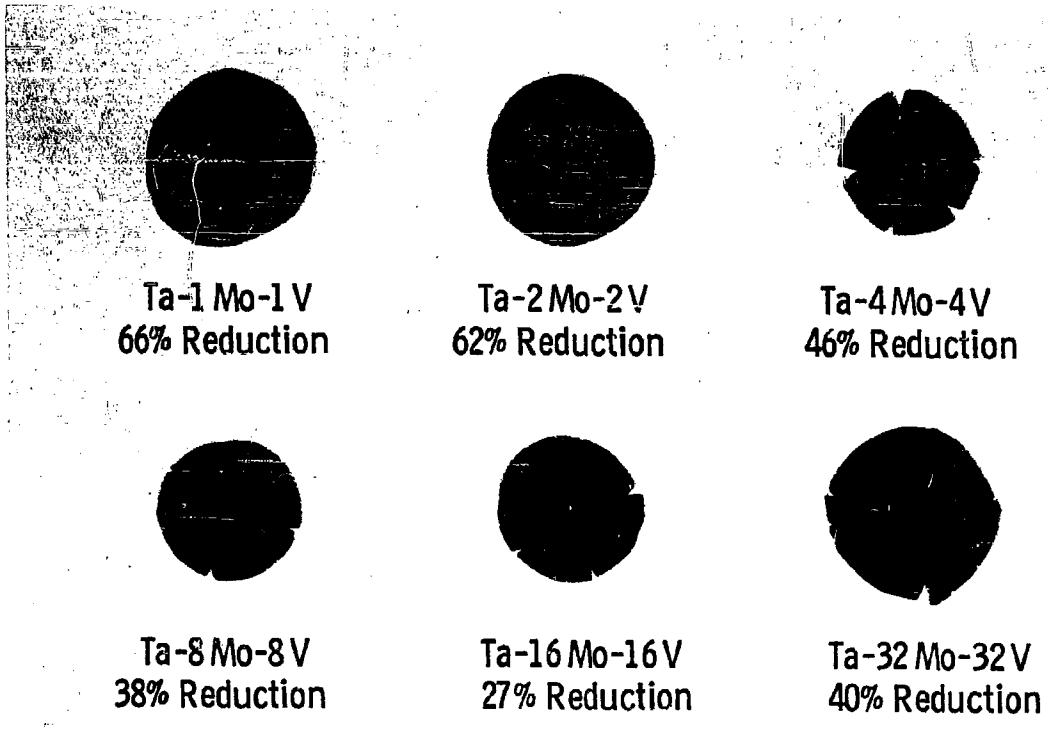

Fig. 33--Arc melted Tantalum - Molybdenum - Vanadium buttons after hammer forging at 1200°C.

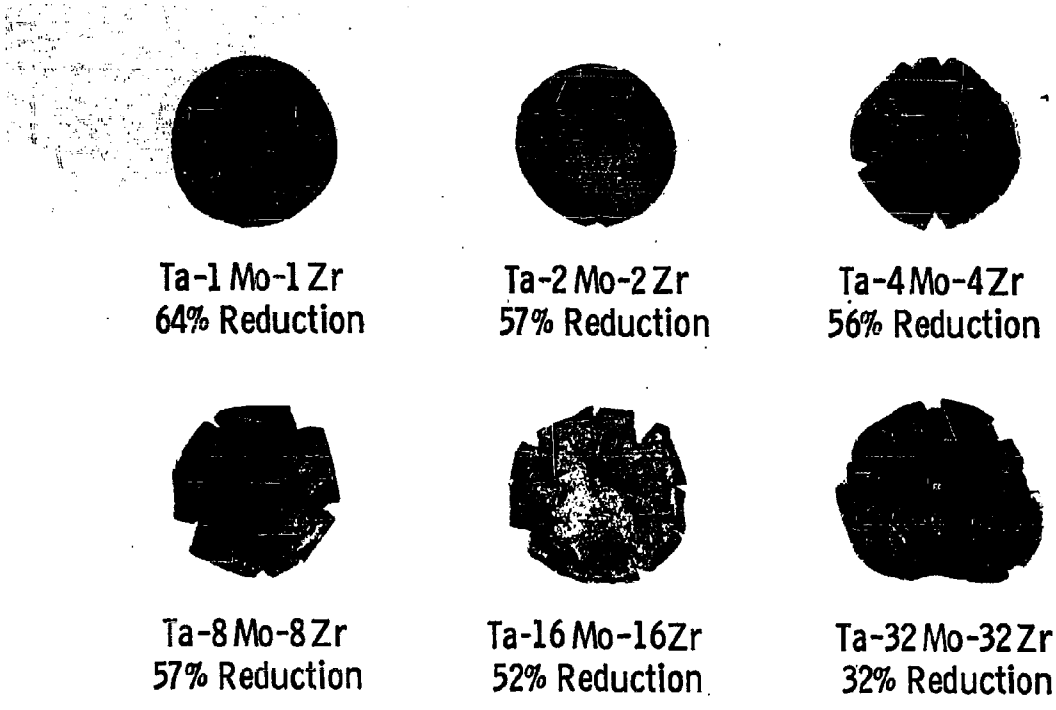

Fig. 34--Arc melted Tantalum - Molybdenum - Zirconium buttons after hammer forging at 1200°C.

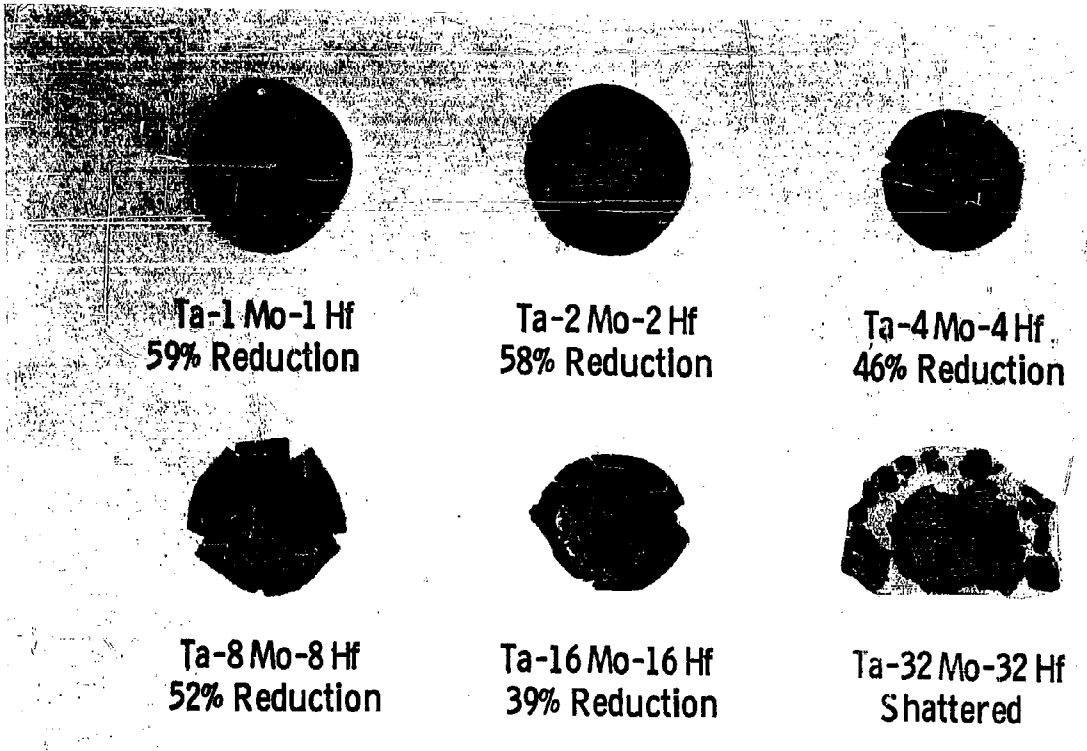

Fig. 35--Arc melted Tantalum - Molybdenum - Hafnium buttons after hammer forging at 1200°C.

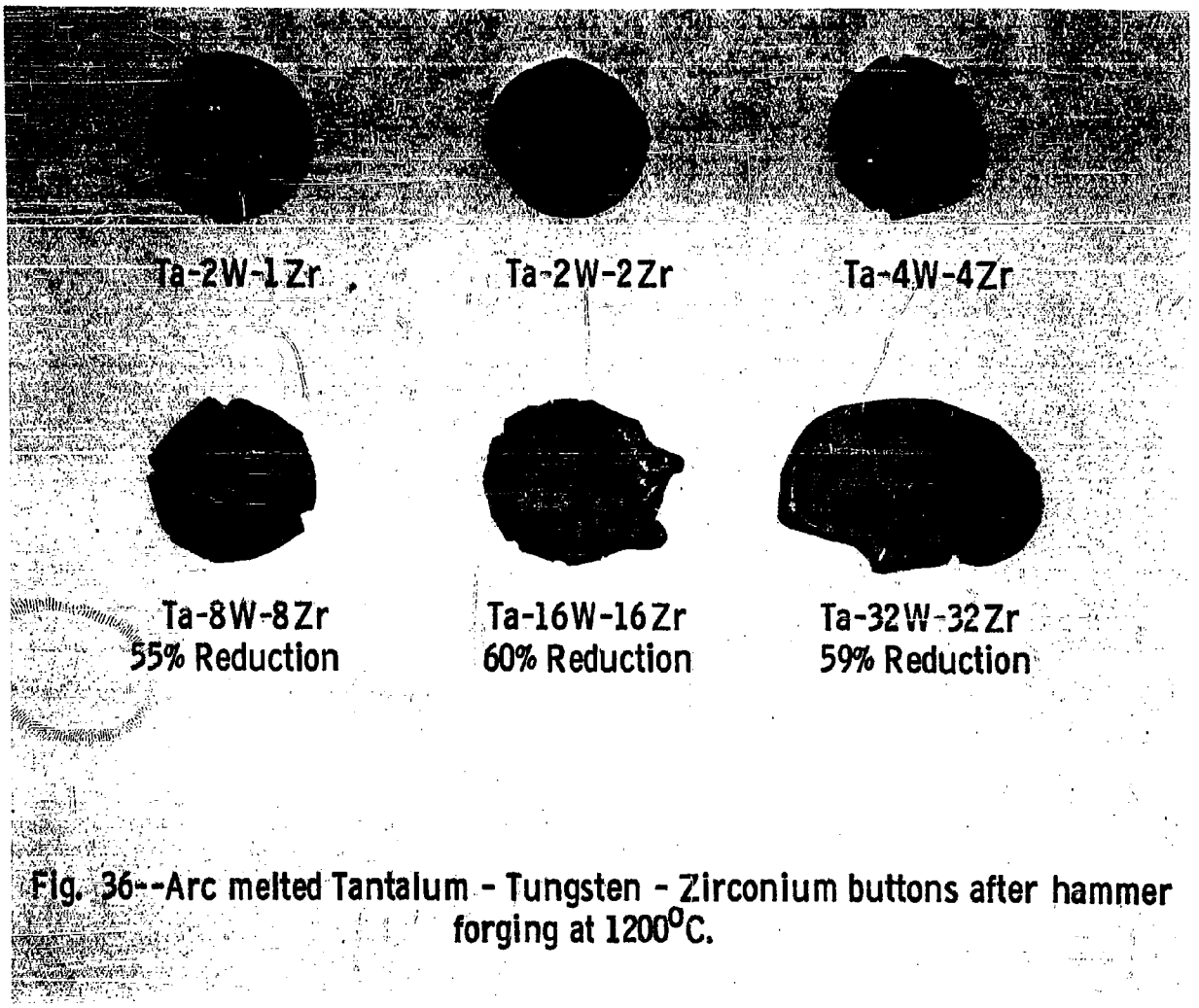

Fig. 36--Arc melted Tantalum - Tungsten - Zirconium buttons after hammer forging at 1200°C.

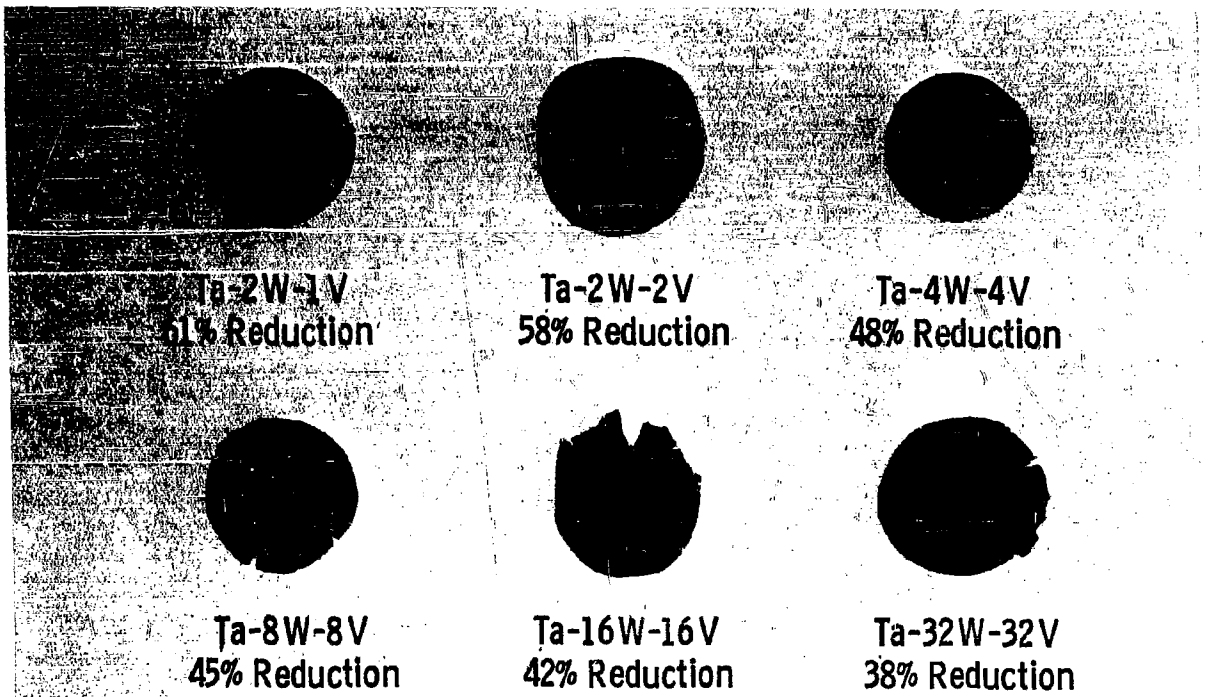

Fig. 37--Arc melted Tantalum - Tungsten - Vanadium bottons after hammer forging at 1200°C.

binary element added. Photographs of several oxidation specimens after exposure are presented in Figures 38-44.

C. HARDNESS TESTING AT SUBZERO AND ELEVATED TEMPERATURES - Elevated temperature hardness was determined for selected Phase I alloys and a number of compositions prepared in Phase III. The test equipment and mounting procedure are described in Appendix A.

All specimens had been annealed for 16 hours at 2000°C. Specimens were tested at 2000°F and in some cases at 1600°F and 2200°F. Results are presented in Table X. Room temperature hardness after the standard annealing treatment of 16 hours at 2000°C are included for comparison.

A Hardness Retention Factor (HRF), defined as the percentage of the room temperature hardness retained at 2000°F, was used to show the influence of the alloying additions. The HRF represents the ability of an alloy to resist softening at elevated temperature. These factors have been computed and included in Table X. For a reference point, pure tantalum has an HRF of 34.

While the HRF was not the only possible criterion for judging the resistance to softening, it provided a quick measure of relative strengthening at room temperature and elevated temperatures. It should be noted that another frequently used criterion, the ratio of alloy hardness to pure metal hardness, is rather closely related to the HRF. In particular, HRF (alloy)/HRF (pure metal) is equal to alloy-metal ratio (2000°F)/alloy-metal ratio (75°F). Thus an HRF greater than that of pure Ta indicates that an alloy is more effective in increasing hardness at high temperatures than it is at low temperatures.

The temperature variation in hardness for Ta-W, Ta-Hf, and Ta-W-Hf alloys is shown in Figures 45-47. Representative Ta-W, Ta-Hf, and Ta-W-Hf alloys are compared in Fig. 48. As expected, additions of Hf and W raise the room temperature and elevated temperature hardness of Ta. Small additions of Hf are more effective than comparable additions of W in resisting softening at 2000°F. Ta-4Hf has an HRF value of 79 compared to 49 for Ta-4W. Ta-W-Hf alloys containing either 2 or 4% Hf combined with 2, 4, or 8% W have HRF values

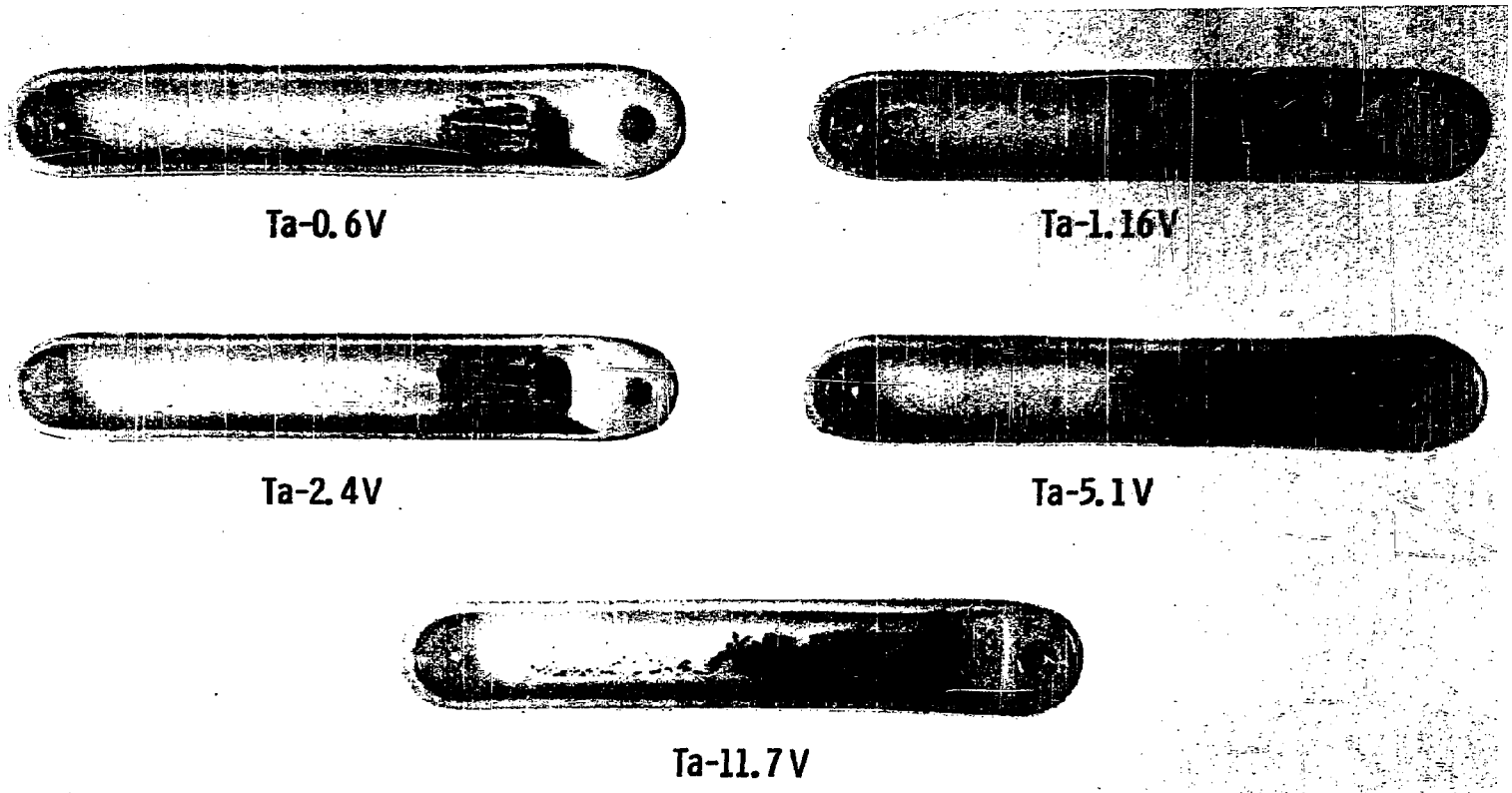

Fig. 38--Oxidation behavior of Tantalum - Vanadium alloys. One hour at 1200°C in still air.

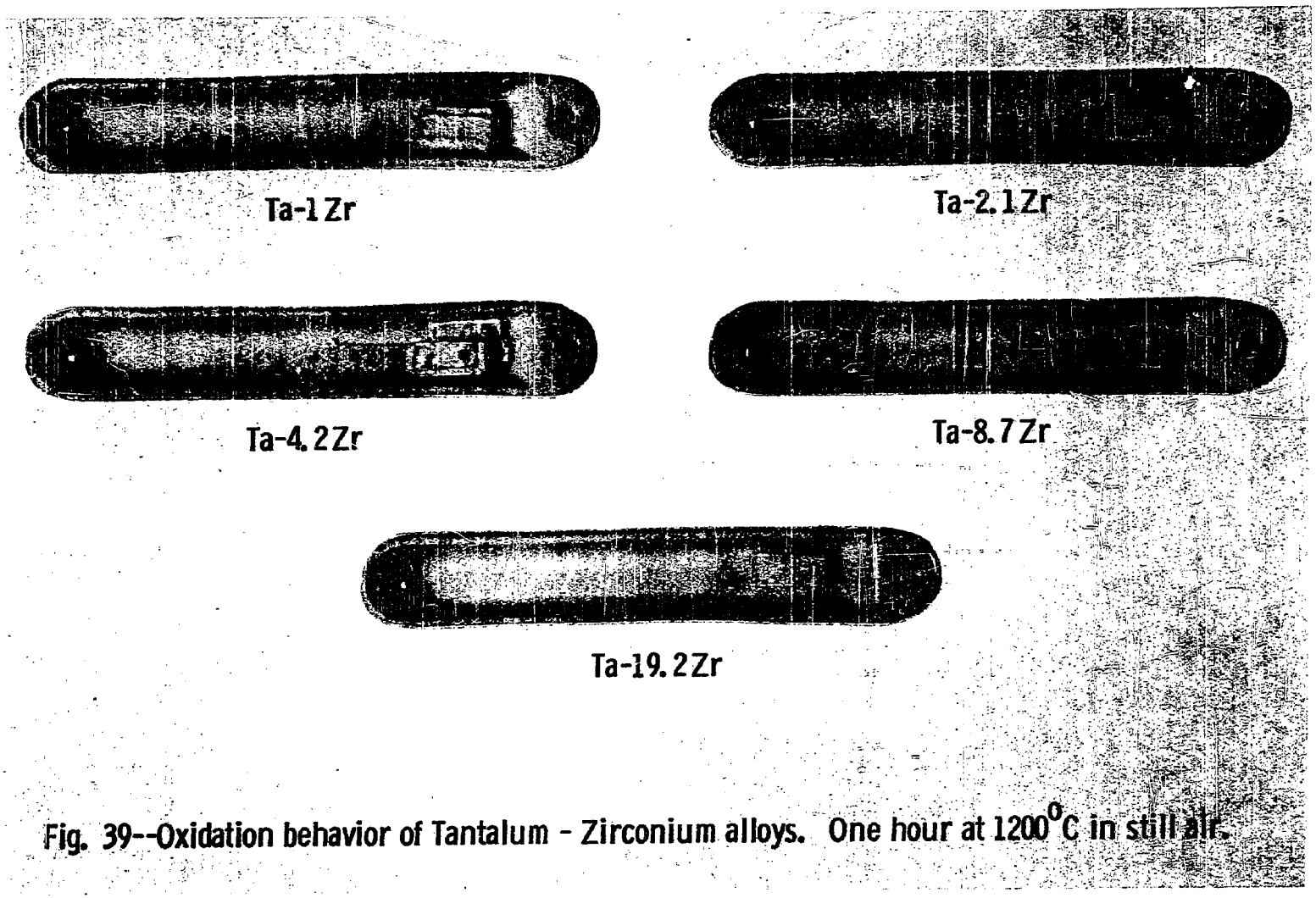

Fig. 39--Oxidation behavior of Tantalum - Zirconium alloys. One hour at 1200°C in still air.

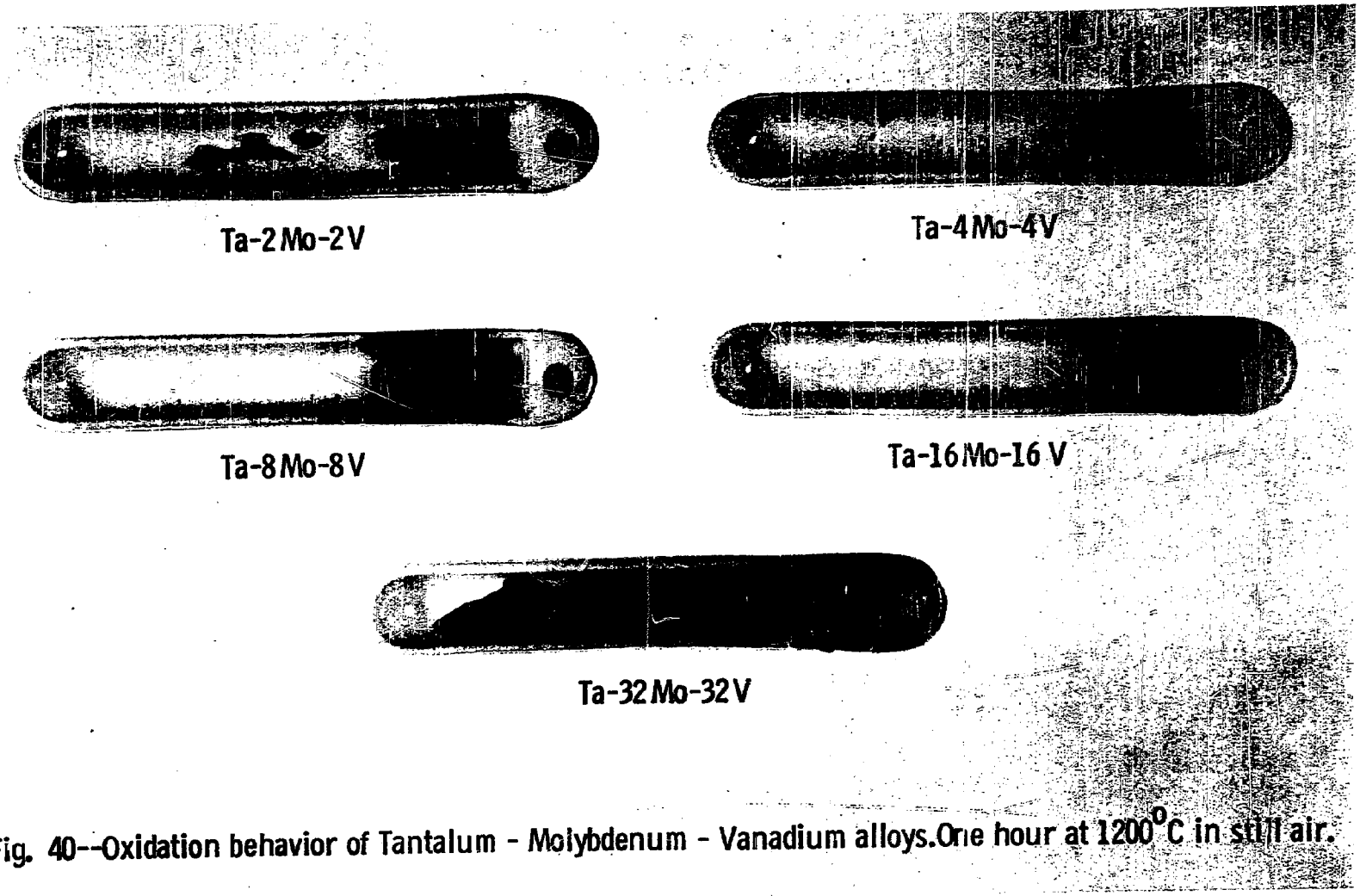

Fig. 40--Oxidation behavior of Tantalum - Molybdenum - Vanadium alloys. One hour at 1200°C in still air.

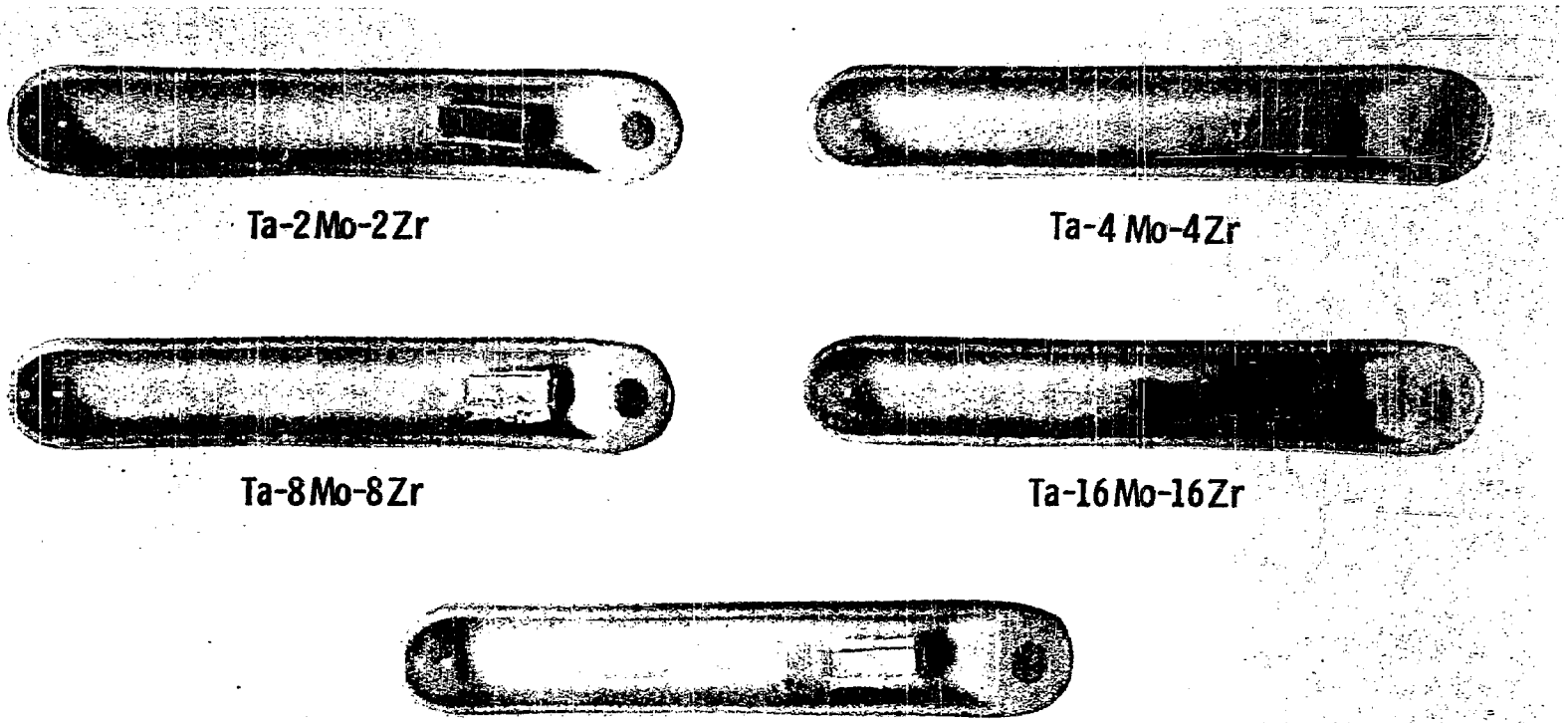

Fig. 41--Oxidation behavior of Tantalum - Molybdenum - Zirconium alloys. One hour at 1200°C in still air.

RM 2285

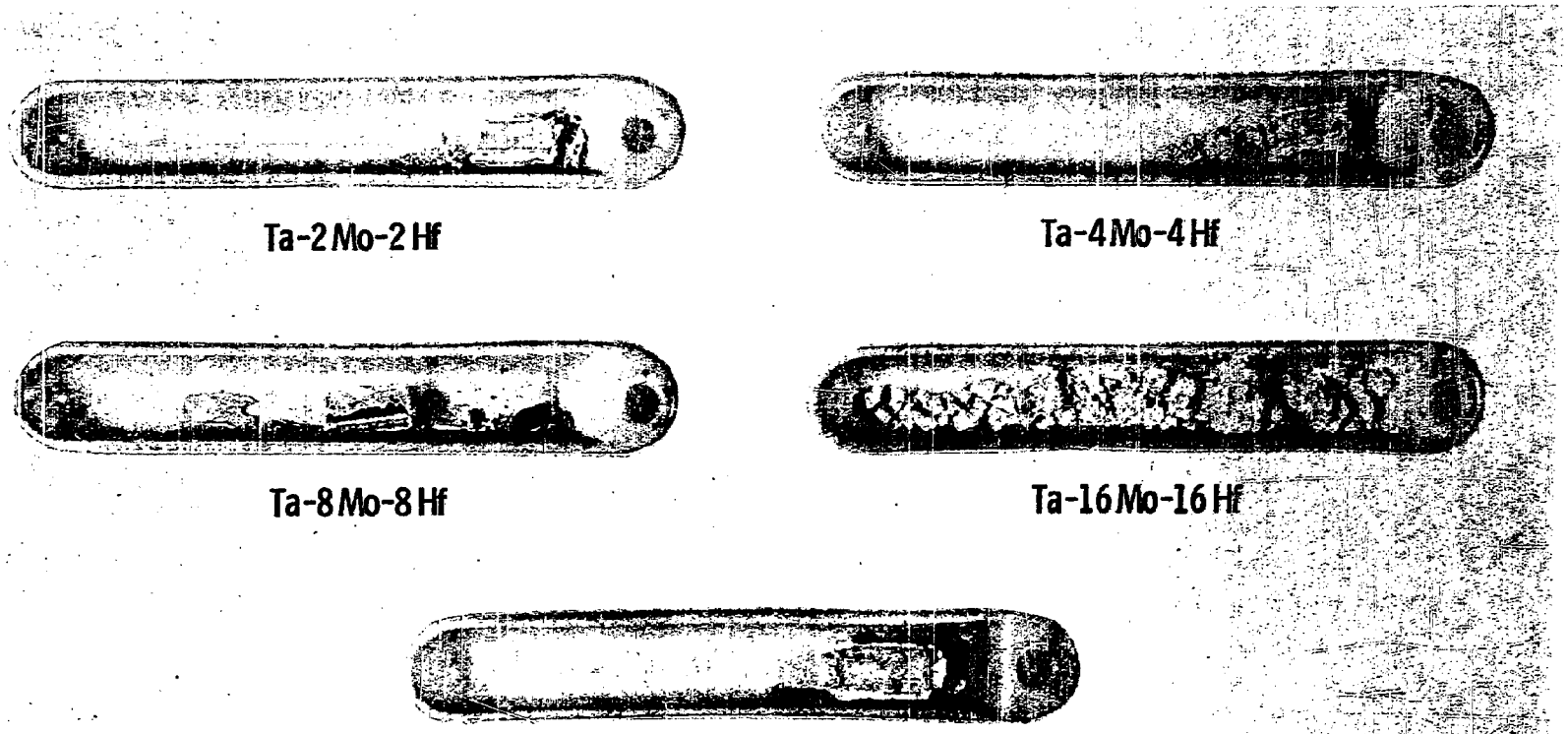

Fig. 42--Oxidation behavior of Tantalum - Molybdenum - Hafnium alloys. One hour at 1200°C in still air.

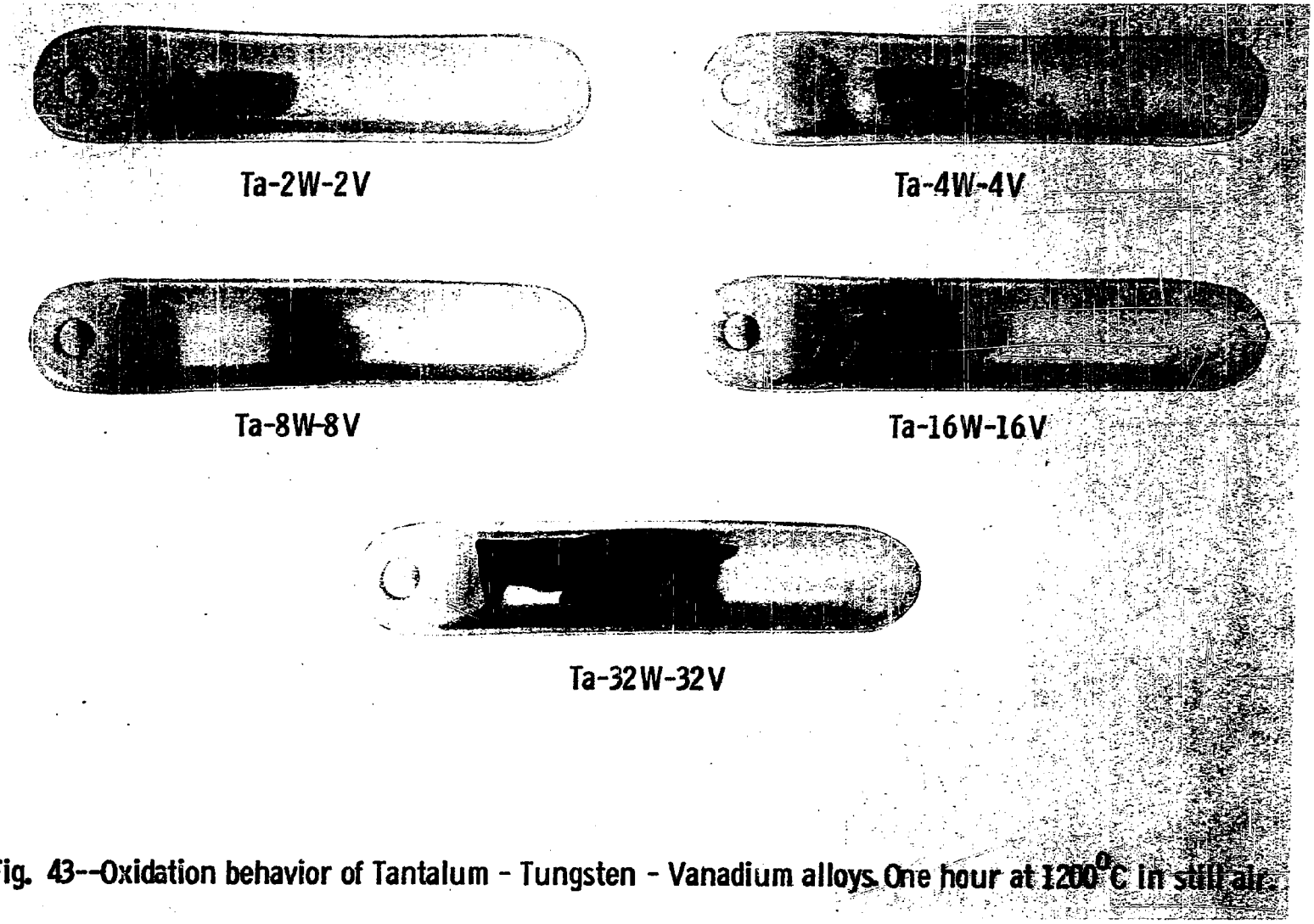

Fig. 43--Oxidation behavior of Tantalum - Tungsten - Vanadium alloys. One hour at 1200°C in still air.

RM 20293

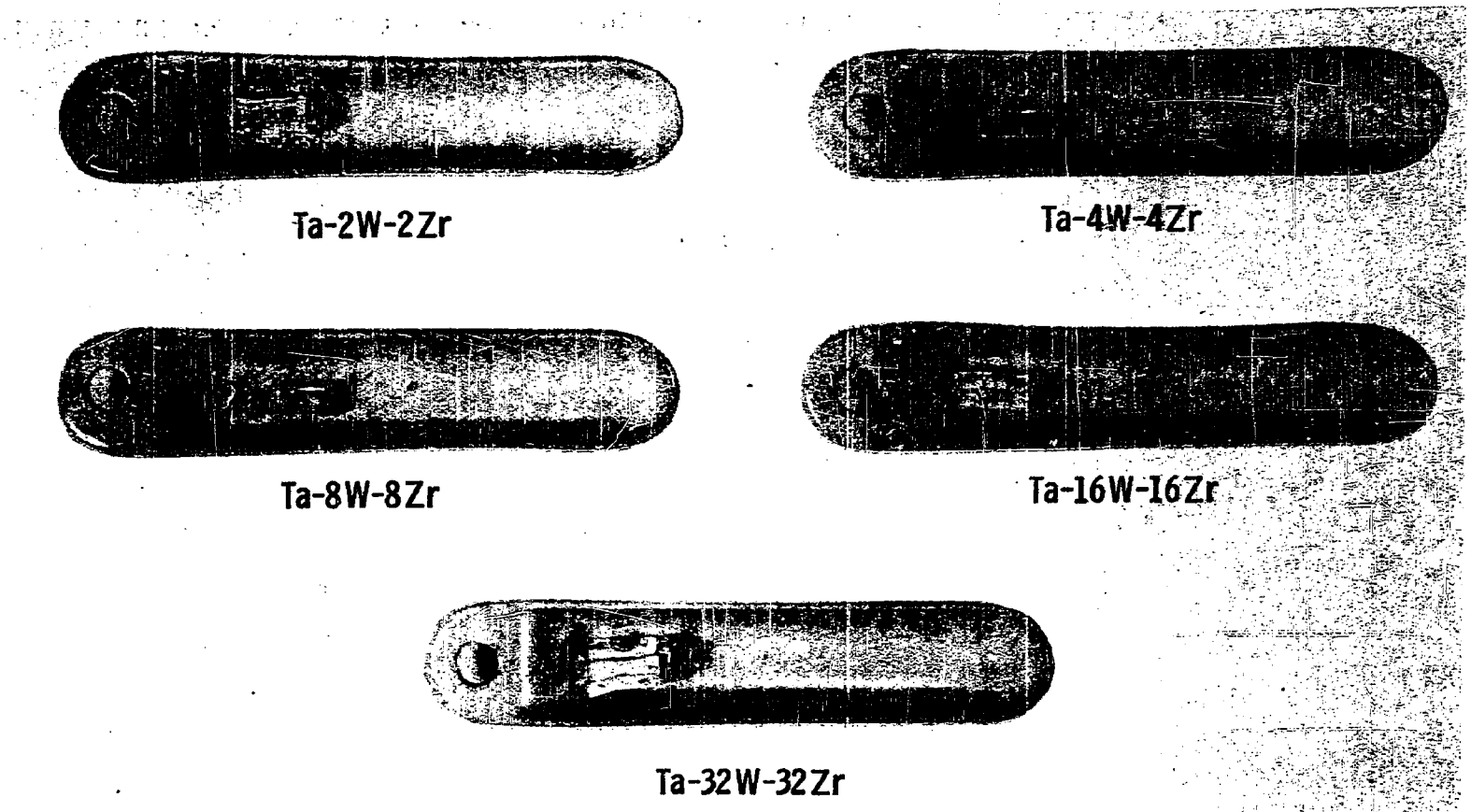

Fig. 44--Oxidation behavior of Tantalum - Tungsten - Zirconium alloys. One hour at 1200°C in still air.

TABLE X

HARDNESS AT ELEVATED TEMPERATURES OF Ta-BASE ALLOYS

Annealed at 2000°C for 16 Hours

Composition	Hardness at Temperature, VHN				HRF(2000°F) /
	75°F	1600°F	2000°F	2200°F	
Pure Ta	125	60	42	-	34
Ta-1Hf	131	-	90	-	69
Ta-2Hf	139	-	91	-	65
Ta-4Hf	158	142	125	-	79
Ta-8Hf	227	152	133	-	59
Ta-50Hf	542	-	166	-	31
Ta-2W	137	80	54	-	39
Ta-4W	175	-	85	-	49
Ta-16W	300	208	153	-	51
Ta-1Re	158	-	60	-	38
Ta-2Re	194	-	73	-	37
Ta-2W-2Hf	213	-	156	-	73
Ta-4W-2Hf	200	163	143	-	72
Ta-8W-2Hf	257	-	207	-	76
Ta-16W-2Hf	316	-	190	-	60
Ta-2W-4Hf	232	192	174	177	75
Ta-4W-4Hf	243	195	212	170	77 *
Ta-8W-4Hf	283	218	212	175	75
Ta-16W-4Hf	348	206	191	182	55
Ta-8W-8Hf	353	-	185	-	52
Ta-2W-2Re	189	144	120	95	64
Ta-2W-4Re	246	-	112	-	46
Ta-4W-4Re	279	-	157	-	56
Ta-8W-4Re	307	-	139	-	45
Ta-4Cb-4Hf	227	-	151	-	67
Ta-4Cb-4Mo	245	-	113	-	46
Ta-4Mo-4Re	352	-	197	-	51

/ $\text{HRF} = \frac{\text{VHN at 2000°F}}{\text{VHN at 75°F}} \times 100$

* Computed on 2000°F Hardness of ~181

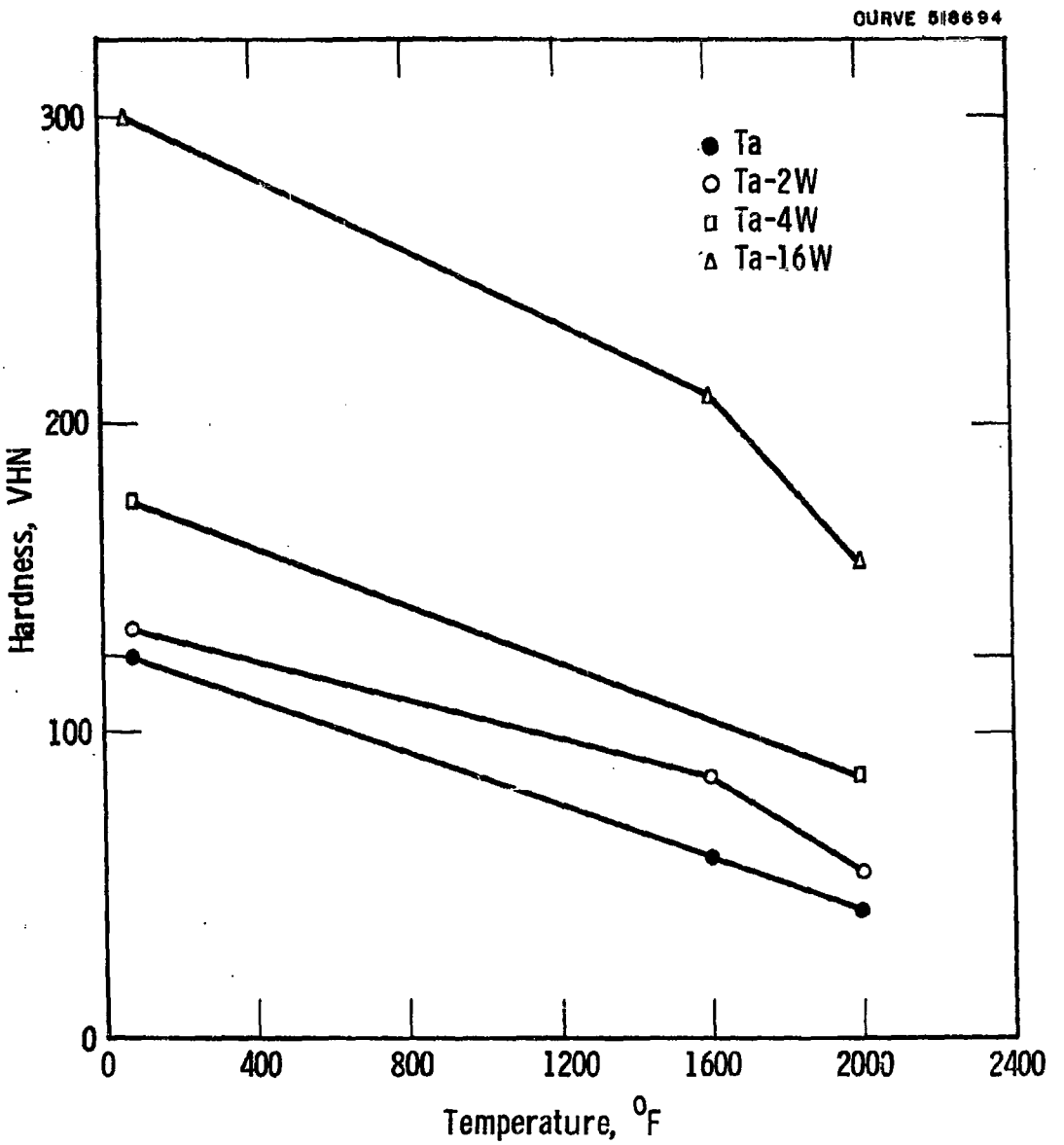

Fig. 45--Temperature variation of hardness for Ta-W alloys

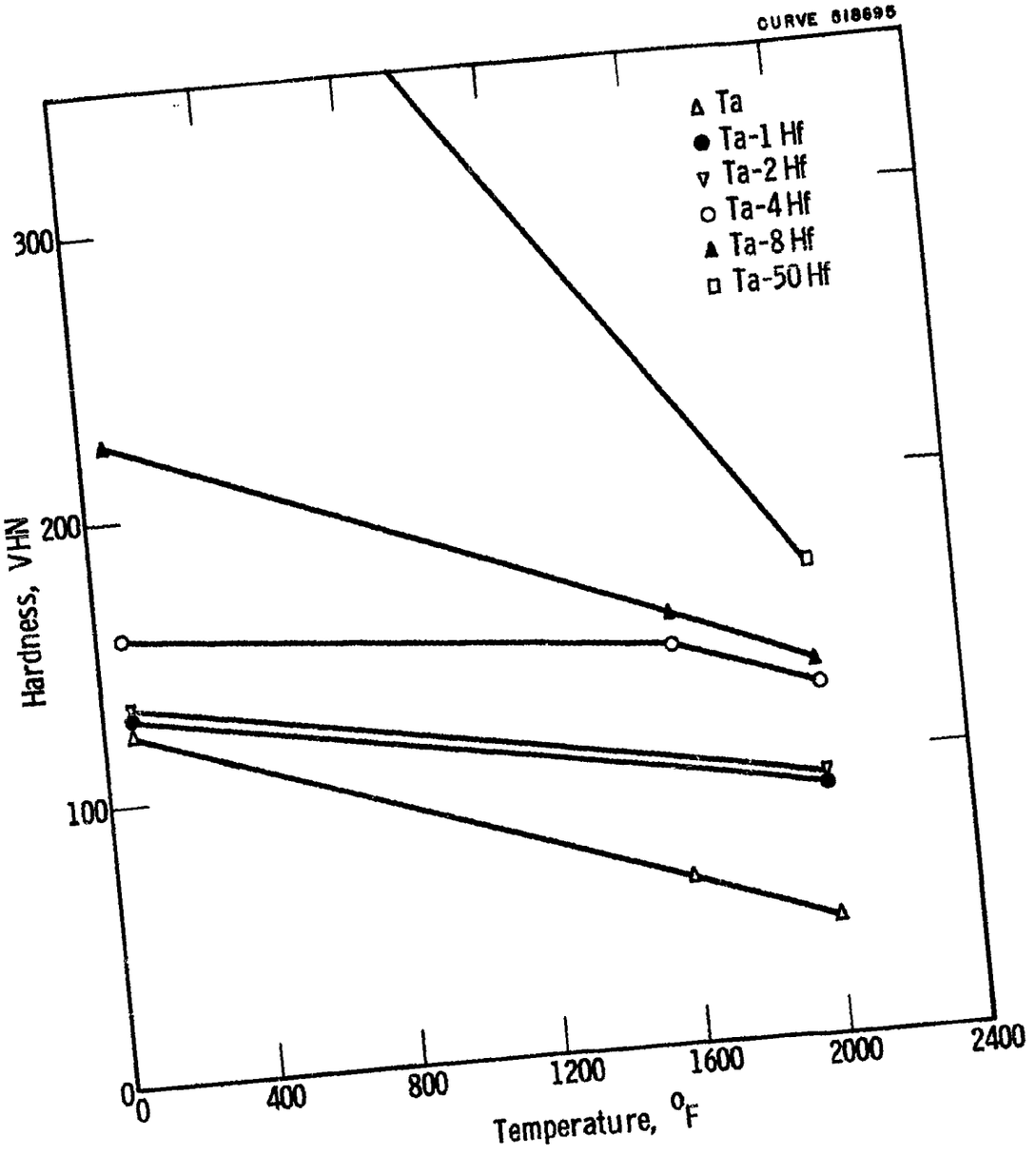

Fig. 46--Temperature variation of hardness for Ta-Hf alloys

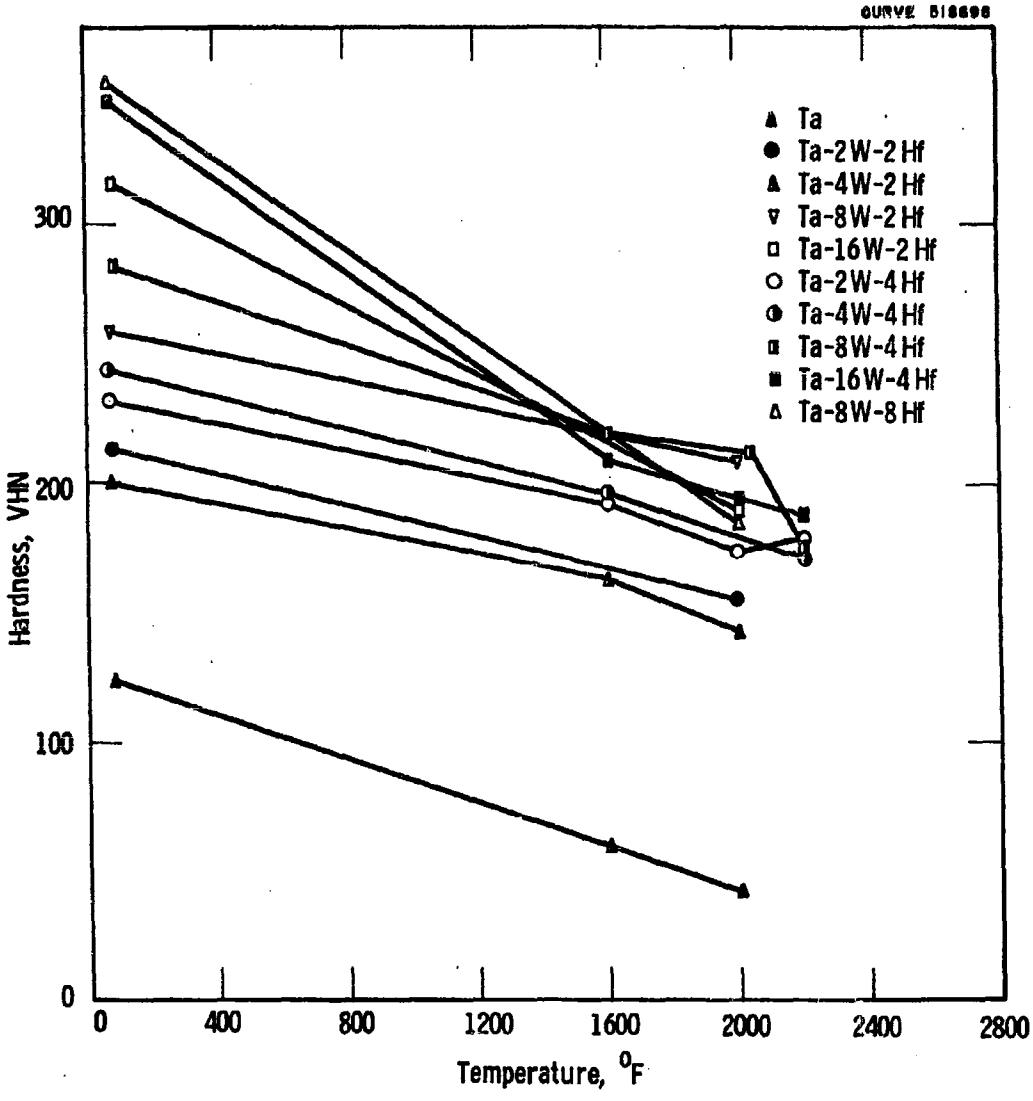

Fig. 47--Temperature variation of hardness for Ta-W-Hf alloys

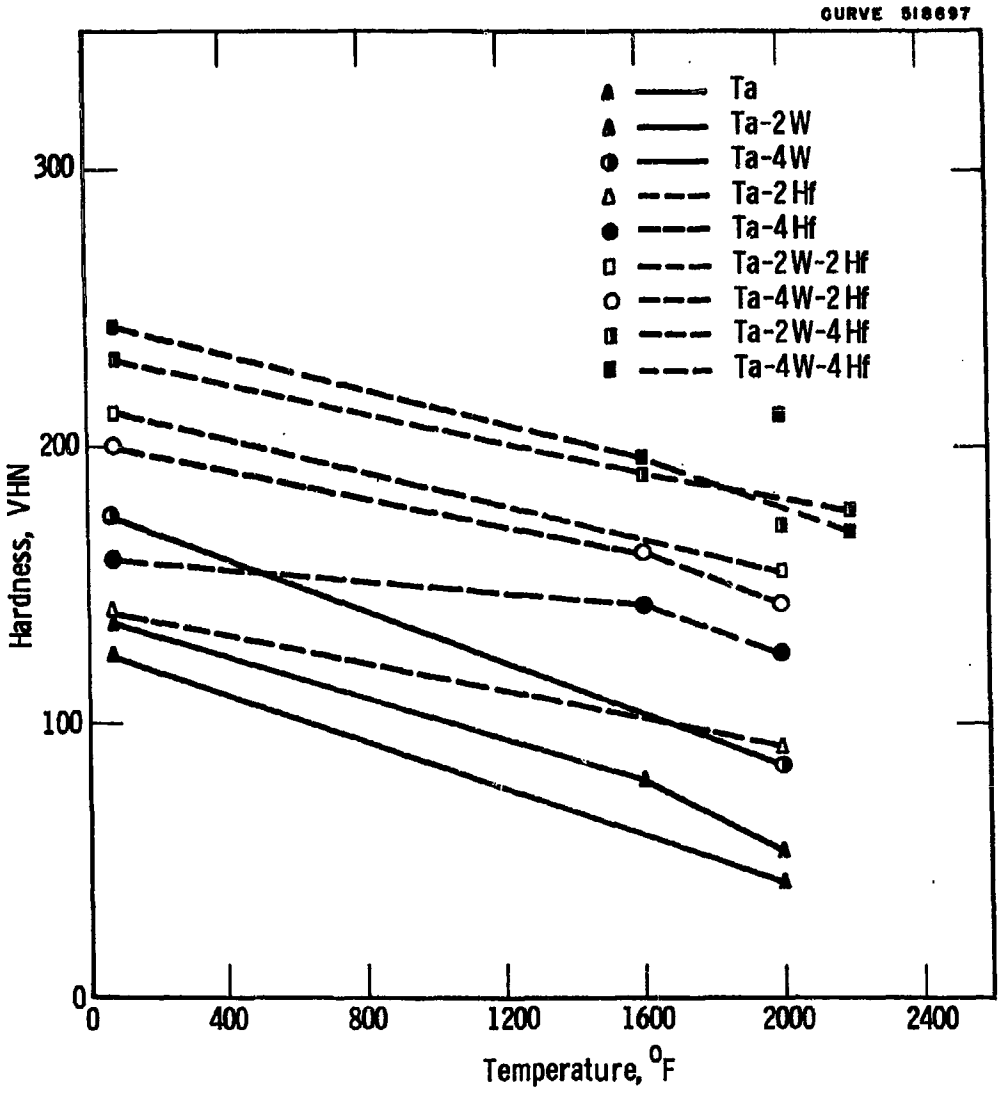

Fig. 48--Temperature variation of hardness for representative Ta-W-Hf alloys

above 70 as well as hardnesses above 140 VHN. Ta-8W-8Hf, Ta-16W-2Hf, and Ta-16W-4Hf alloys have lower HRF values of 52, 60, and 55 respectively, in the same range as those for the Ta-W alloys, although the hot hardness remains quite high. These results indicate that additions of Hf to Ta ranging up to 4% are highly effective in resisting softening at 2000°F, while additions of 8 or 16% Hf are less effective, being comparable to the effect of tungsten additions.

The temperature variation of hardness for Ta-Re and Ta-W-Re alloys are shown in Fig. 49. Small additions of Re (1 and 2%) and W (2%) have essentially no effect upon the ability of tantalum to resist softening at 2000°F. Combinations of these elements offer moderate to good improvement in softening resistance. Ta-2W-2Re has the best hardness retention, as measured by HRF, of the Ta-W-Re alloys tested. Ta-4W-4Re is better than Ta-4W-8Re or Ta-4W-2Re, but is not as good as Ta-2W-2Re. None of these alloys are as good as the Ta-W-Hf alloys either in HRF or in high temperature hardness.

Room temperature and 2000°F hardnesses were obtained for a few additional alloys to determine the effect of replacing W with Cb in a Ta-W-Hf alloy and W with Mo in a Ta-W-Re alloy. A Ta-Mo-Cb alloy was also examined to have a comparison with an alloy containing neither W, Re, or Hf. Hardness values are presented for these alloys, Ta-4Cb-4Hf and Ta-4Mo-4Re, in Fig. 50 together with similar data for Ta, Ta-4W-4Re, Ta-4W-4Hf, and Ta-4Mo-4Cb. The room and elevated temperature hardness level of Ta-4Hf-4W is reduced slightly by replacing W with an equal amount of Cb. The HRF is also lowered from 77 to 67. Comparison of the hardness and HRF values for Ta-4W-4Hf, Ta-4Cb-4Hf with those for Ta-4Cb-4Mo indicate that Hf has an appreciable effect upon hardness retention at elevated temperatures. The rate of decrease of hardness with temperature is far less for the alloys containing hafnium. This is illustrated in Fig. 50 by the relative slopes of the hardness vs temperature curves as well as by the HRF values. The hardness of Ta-4Cb-4Hf drops 76 VHN between room temperature and 2000°F while Ta-4Cb-4Mo decreases 132 VHN. The corresponding HRF values are 67 and 46.

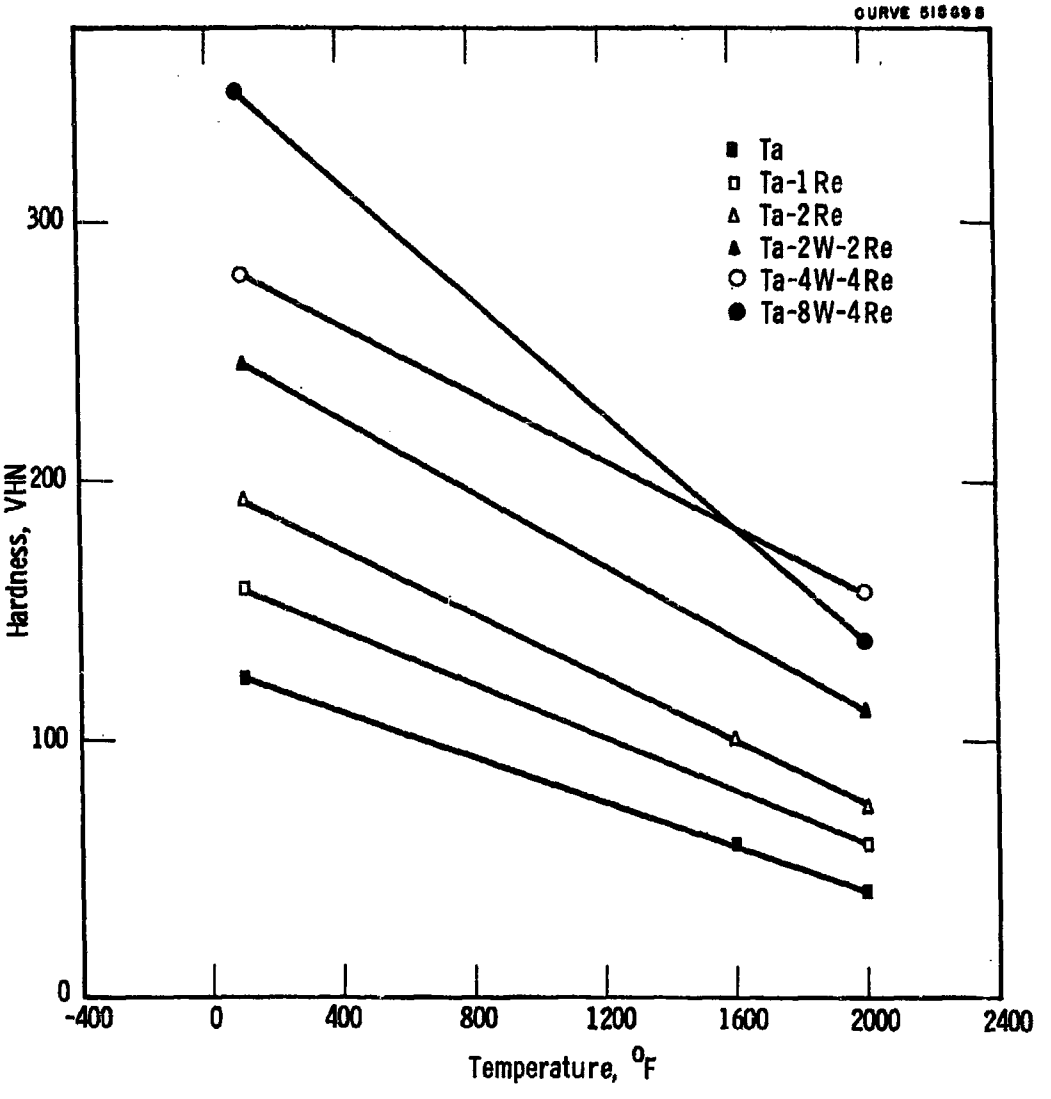

Fig. 49--Temperature variation of hardness for Ta-W-Re alloys

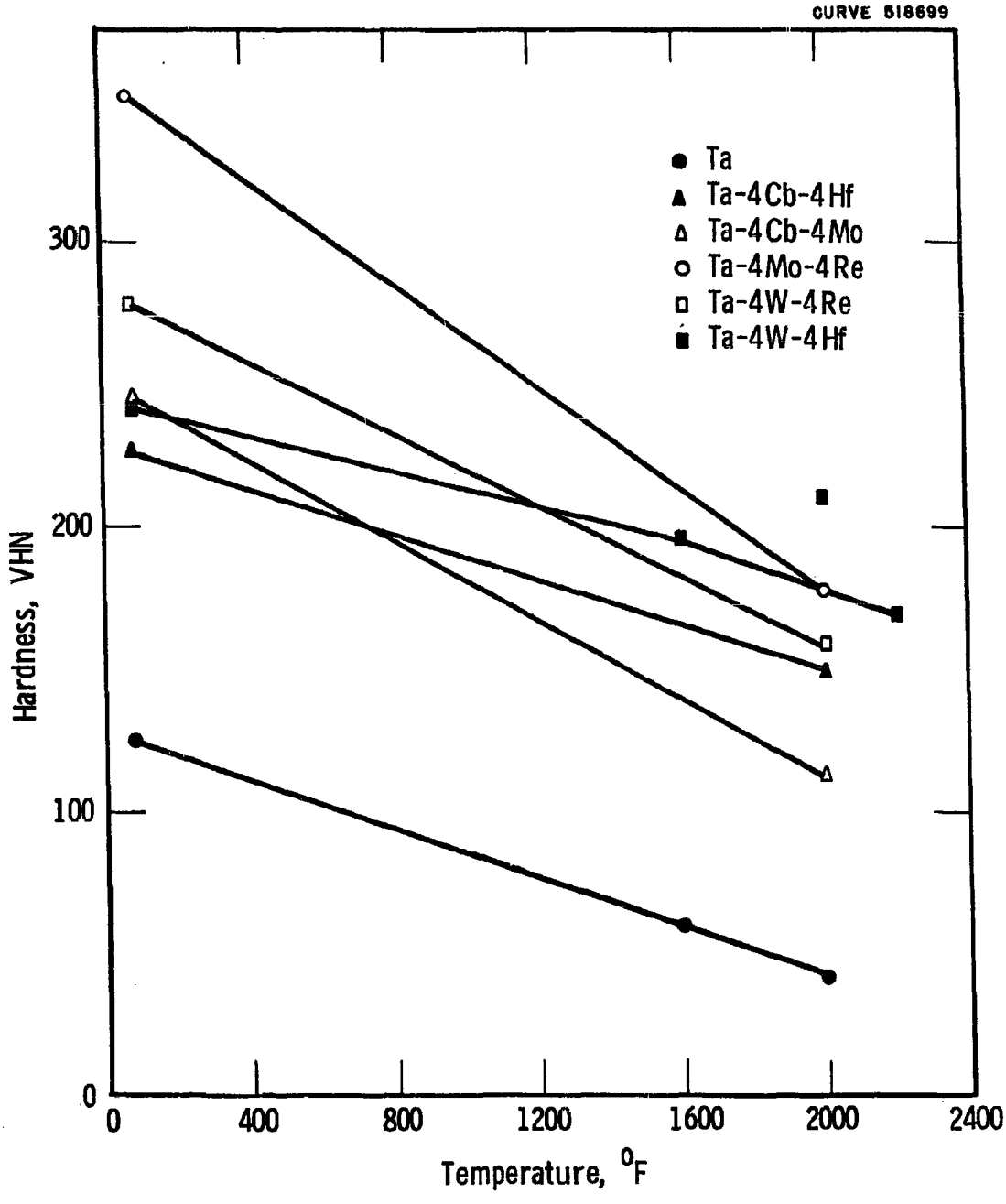

Fig. 50--Temperature variation of hardness for Ta base alloys

Table XI presents subzero, room, and elevated temperature hardness data for W-Re, W-Ta-Re and W-Cb-Re alloys. These results illustrate the two-fold effect which Re has upon the hardness of tungsten when added alone or with Ta or Cb. This element decreases room temperature hardness and substantially improves the resistance to softening at elevated temperatures of tungsten base alloys. The addition of 8% Re to W decreases room temperature hardness about 50 VHN and increases 2000°F hardness over 20 VHN. The HRF changes from 20 to 30. Combinations of Ta and Re are even more effective in increasing the resistance to softening at 2000°F. W-4Ta-8Re has an HRF of 61 compared to 21 for pure W, 31 for W-8Re and 47 for W-4Ta-4Re. A small addition (2%) of tantalum improves the HRF of a W-Re alloy drastically, while further additions have very little effect.

As mentioned previously, Re in amounts up to 6-8% reduces the room temperature hardness of W. To study this effect further, hardnesses at and below room temperature were obtained for W base alloys containing Re with and without additions of Cb or Ta. A Vickers hardness tester equipped with a cold chamber enabled hardnesses to be obtained between room temperature and liquid nitrogen temperatures. (See Appendix A) A standard load of 20 kg was used, and hardness was computed in the normal manner.

The effect of Re additions upon the hardness of tungsten at room temperature is shown in Fig. 51. This figure includes hardness values for both arc melted and annealed (16 hours at 2000°C) 20 gram buttons. Although there is scatter in the data, a distinct decrease in hardness to a minimum at 6-8% Re occurs. At lower temperatures the effect is even more pronounced. At -325°F, the hardness of W is decreased 380 VHN when Re is increased from 2 to 8%, as shown in Fig. 52. Figures 53 and 54 illustrate the effect of the additions upon the hardness of W-Ta and W-Cb alloys, respectively. Re additions continue to reduce the general hardness level of W with Ta or Cb present. Cb or Ta additions at constant Re level increase hardness at all test temperatures.

If the effects at high and low temperatures are considered jointly it is obviously possible to have an alloy which is softer at room temperature while being considerably harder at elevated temperatures than pure tungsten.

TABLE XI

HARDNESS OF W-BASE ALLOYS AS A FUNCTION OF TEMPERATURE

Annealed at 2000°C for 16 Hours

Composition	Hardness at Temperature in °F, VHN								HRF(2000)
	-325	-240	-150	-60	75	1600	2000	2200	
Pure W					337		70		21
W-1Re					333		67		20
W-2Re	954		577	448	335		81		25
W-4Re	737		519	388	292				
W-6Re	639		502	401	299				
W-8Re	574		476	371	298		91		31
W-10Re	630		455	385	326				
W-16Re					517				
W-24Re					599				
W-32Re					618				
W-2Ta-2Re		659	546		330		145	132	44
W-4Ta-2Re		662	562		350	145	122		35
W-2Ta-4Re		609	517		320		164		51
W-4Ta-4Re		628	534		329		156		47
W-8Ta-4Re		651	577		346				
W-4Ta-8Re		584	485		322		201		63
W-8Ta-8Re		651	577		346				
W-1Cb-2Re		643	521		351				
W-2Cb-2Re		670	558		350				
W-1Cb-4.1Re		588	496		302				
W-2Cb-4.1Re		658	552		324				
W-4.1Cb-4.2Re		574	566		365				
W-2Cb-8.3Re		609	486		331				
W-4.1Cb-8.4Re			540		353				

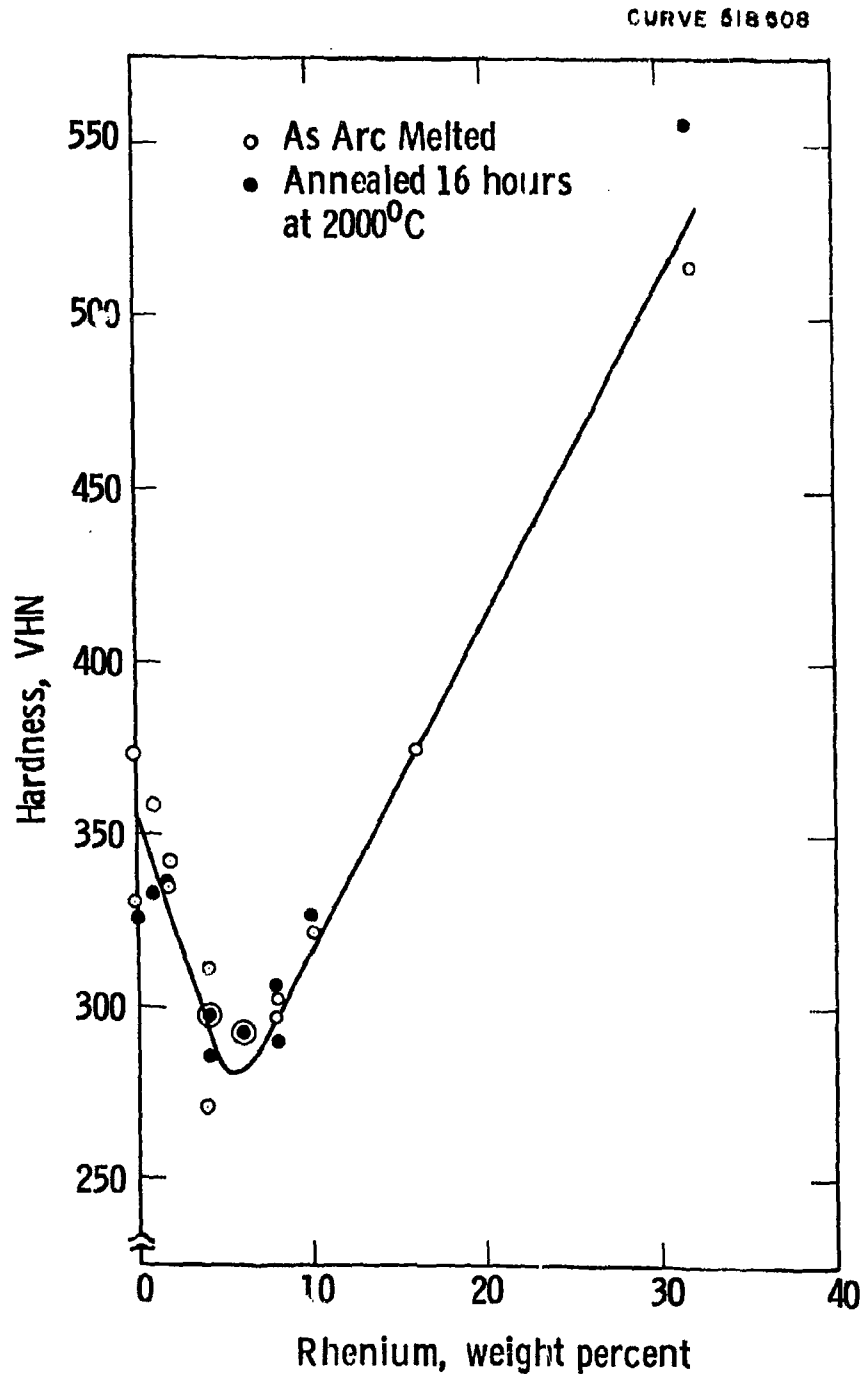

Fig. 51--Hardness of Tungsten-Rhenium alloys at room temperature

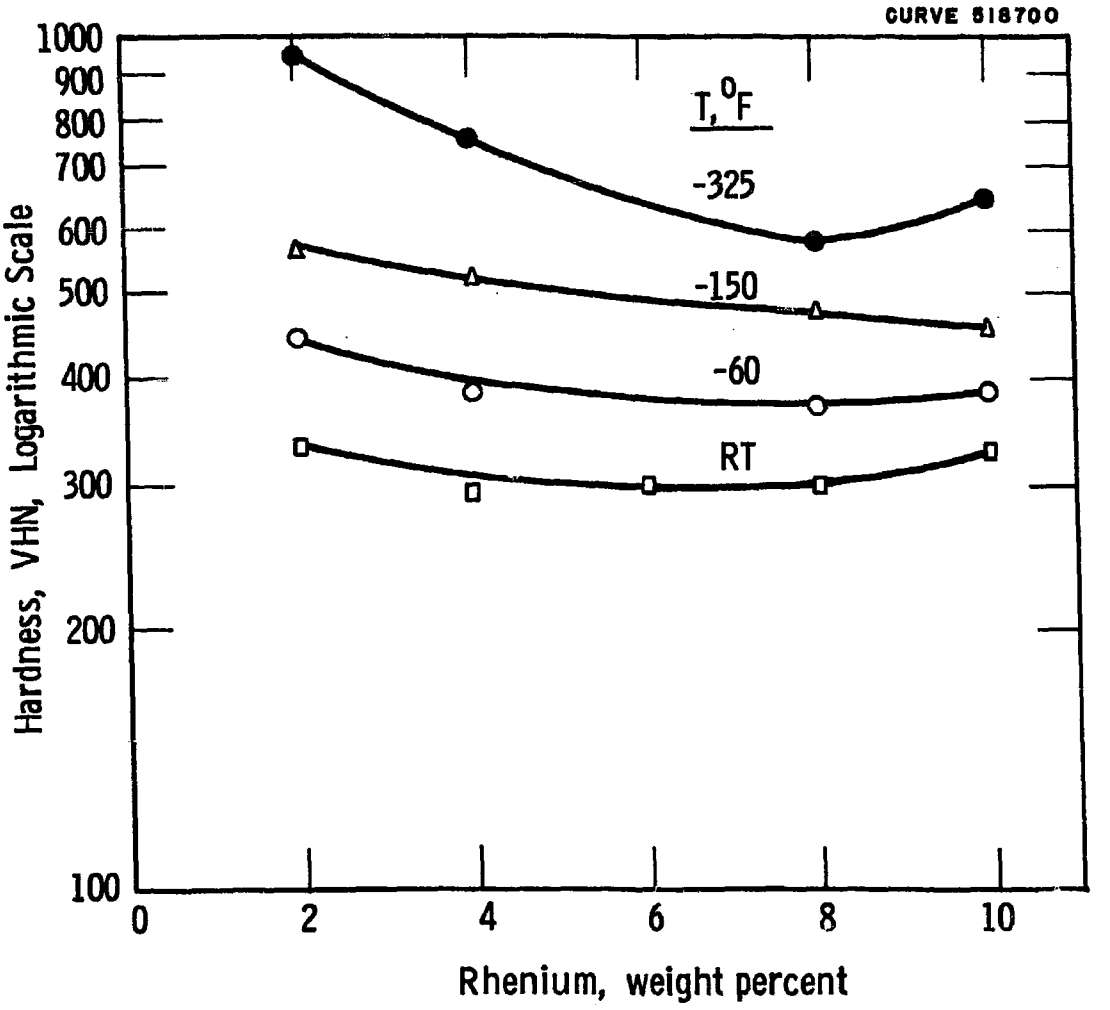

Fig. 52--Hardness of W-Re alloys as a function of temperature

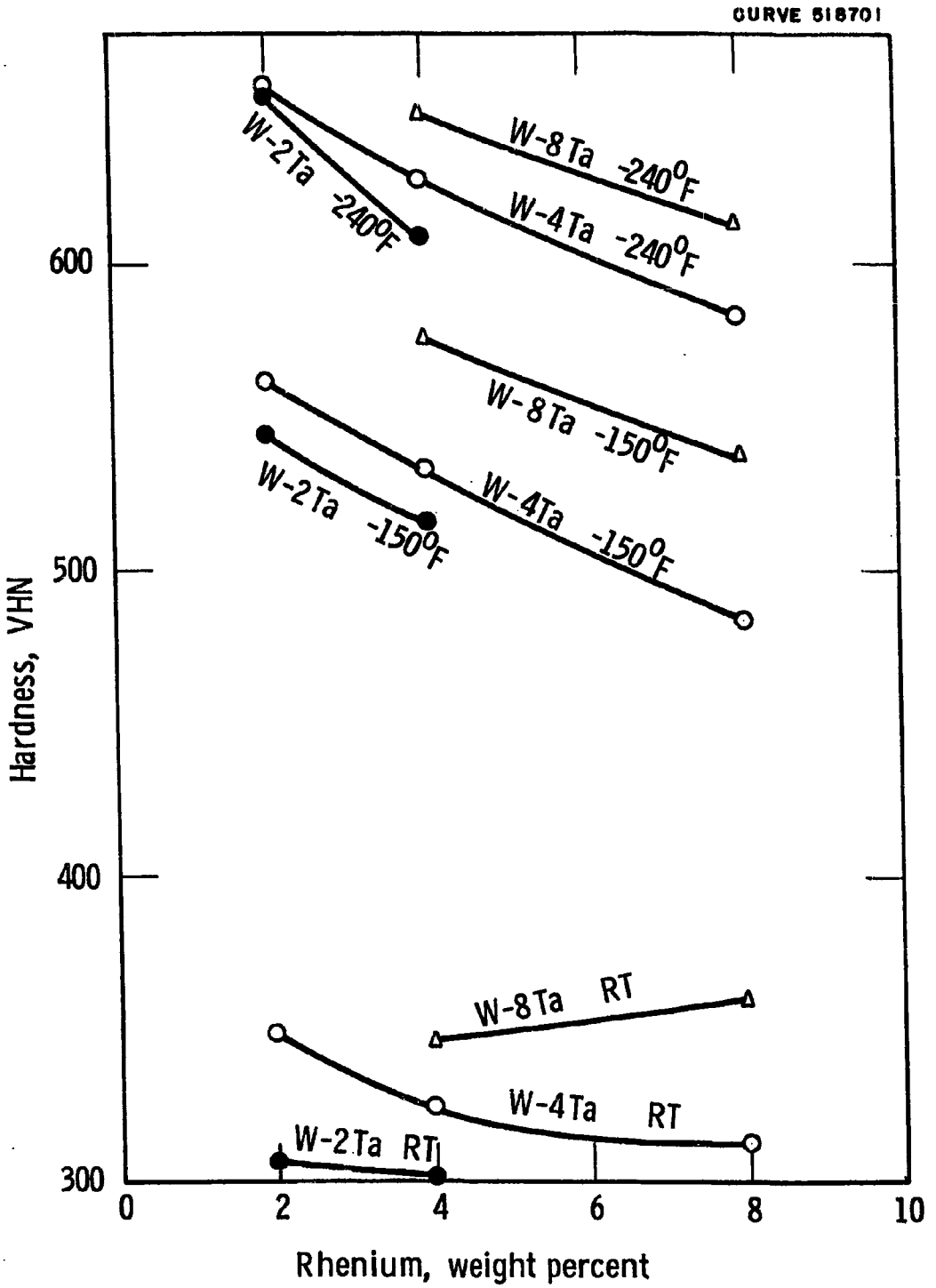

Fig. 53--Hardness of W-Ta-Re alloys as a function of temperature

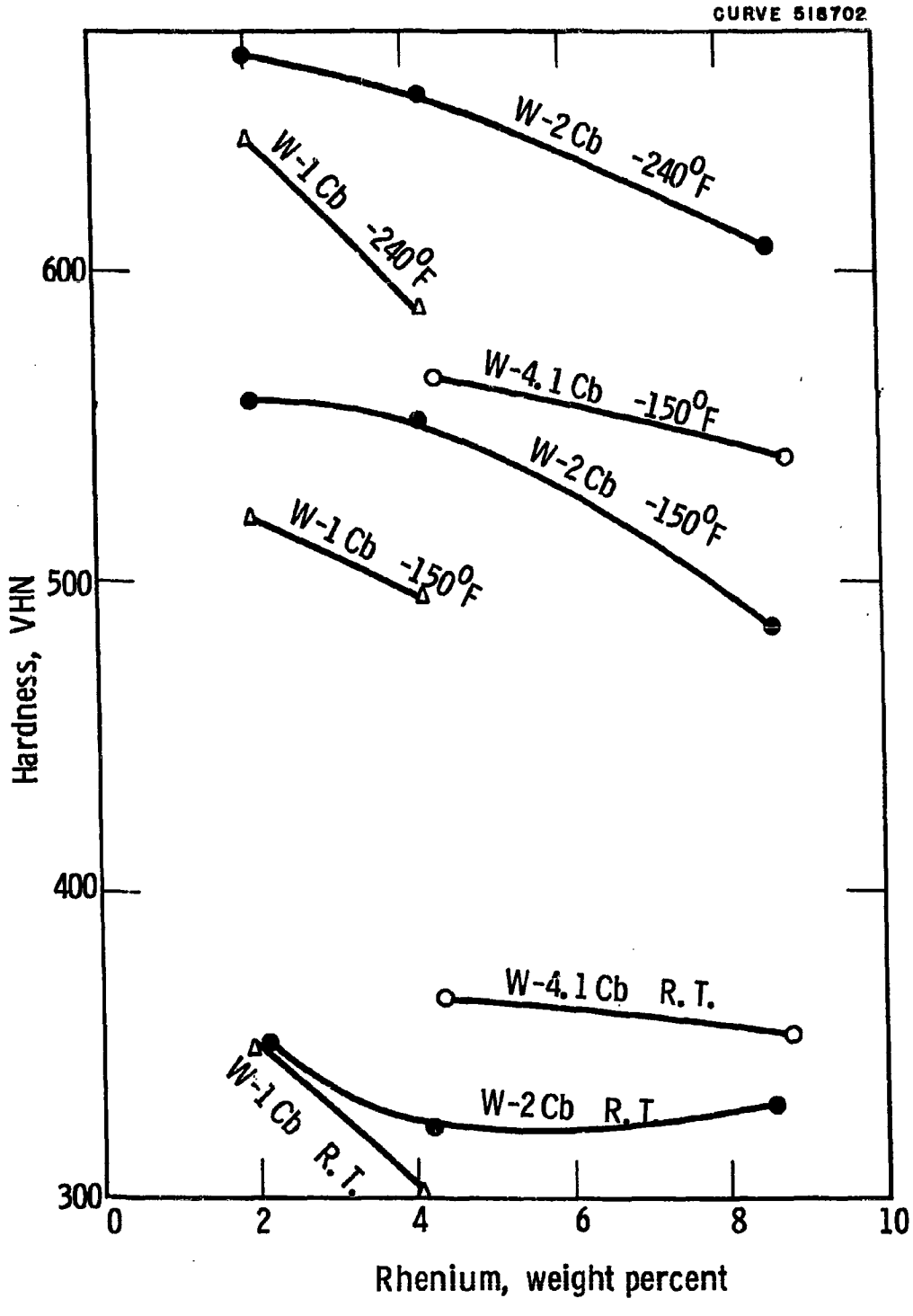

Fig. 54--Hardness of W-Cb-Re alloys as a function of temperature

D. PHASE II - SCALE-UP DEVELOPMENT -- On the basis of available data from Phase I and Phase III alloy screening studies, a number of compositions which appeared to offer property improvement were selected for production of pilot ingots. These were the following:

Ta	Ta-8W-8Hf
Ta-10W	Ta-8W-8Hf-0.1C
Ta-2W-2Hf	Ta-10W-10Hf
Ta-5W-5Hf	Ta-4W-4V
Ta-7.5W-5Hf	Ta-4W-4Hf-4Re
Ta-6W-6Hf	

Alloy materials were pressed into consumable electrode bars and single arc melted in high vacuum to produce ingots of 2 inch diameter weighing approximately six pounds. A DC power supply was employed initially for melting and later an AC system was installed. The furnace is described in Appendix A.

The first procedure used to prepare tantalum alloy electrode bars for consumable arc melting involved efforts to press mixtures of powders and metal rods simultaneously into dense shapes. The desired alloy additions were selected in the purest form available, whether powder, sponge, rod or sheet trimmings. These additions were then incorporated into the tantalum powder base by distributing them as uniformly as possible in the pressing die cavity. Rods were laid lengthwise along the central axis. A hydraulic press was used to impress a total of 550 tons pressure on an area of 15 square inches (20" x 3/4" x 3/4"). This averaged out to about 37 tons/in^2 pressure. Outgassing and some sintering was accomplished by heating the bar within an induction coil in vacuum at 1600°C for 2 hours. The coil was vertical and the bar was merely suspended by a tungsten wire in the center of the coil.

Tungsten electrodes were purchased as 5/8" diameter sintered and swaged bars and were used directly in this form for the preliminary melting work. Later in the program, a tungsten alloy was prepared by slotting a tungsten bar longitudinally and press fitting an alloy rod into the slot.

The pressed tantalum electrode bars of 20" x 3/4" x 3/4" size were argon-welded to columbium adapters designed for use in the vacuum arc furnace.

The purpose of the adapter was to permit maximum melting of the electrode, thereby giving 90-95% yield from electrode to ingot.

When DC melting of these tantalum alloy bars was attempted, two major troubles were encountered:

(1) The resistance heating of the electrode, caused by the passage of large currents, resulted in the generation of extremely high electrode temperatures. The electrode became white hot, warped, and subsequently contacted the sidewall of the crucible. This required immediate shutdown of the melting operation. Also, interior furnace components were damaged by radiant heat from the electrode, necessitating frequent repairs or replacement of parts.

(2) Alloy additions in the form of rods, especially of lower melting point reactive metals, melted prematurely ahead of the arc and ran out of the interior of the electrode. This produced large cavities in the electrode structure and made arc stability difficult to maintain. Also, it was impossible to produce a homogeneous ingot in this manner.

The first of these difficulties required changes in furnace design and improvement of electrode pressing technique. Furnace revisions included (a) addition of an extra 12" length of water-cooled jacket in the melting chamber section to permit absorption of radiant heat from the electrode, (b) replacement of flat steel springs in the water hose guide assembly in the tower by cable-type spring motors which were heat insensitive, and (c) rearrangement and enlargement of sight ports to improve visibility. These changes permitted operation at high DC power without further failure of furnace components. To alleviate the electrode warpage problem, higher compacting pressures were used. A longer sintering time in vacuum at 1600°C was tried, with hopes of increasing outgassing and promoting greater electrode density. These changes in electrode preparation method did not improve the ability to melt tantalum alloys with DC power.

The second difficulty mentioned above, which involved premature melting of alloy additions in rod form, required another type of alloy addition method to eliminate the use of rod material. The primary trouble had been with iodide hafnium rods, and it was decided to use a powdered hafnium hydride as an addition, thereby providing improved compatibility with the tantalum powder base. To do this, iodide hafnium rod was hydrided, crushed to a fine powder, and incorporated in the electrode. The hafnium hydride was then decomposed during the vacuum sintering of the electrode and the hydrogen pumped off.

To increase density of the electrodes and improve the sintering of pressed material, a facility (Kennametal, Inc.) having a 1000-ton hydraulic press and excellent sintering facilities co-operated in preparation of electrodes. The same size electrodes were pressed as before (20" x 3/4" x 3/4"), but a total pressure of 750 tons was used. The bars were then sintered in an induction heated susceptor type furnace at 1600°C for 2 hours, with the total heating and cooling cycle requiring 24 hours. This treatment produced straight bars of greater density than the previous method. No warpage was encountered during the subsequent melting operations.

Despite the improvements in performance of the furnace and of the electrode stock from these modifications, it was still not possible to melt 2" diameter ingots of tantalum alloys or tungsten in any reproducible manner. It was decided to install an AC power supply in hopes that the majority of problems could be eliminated. Two 60-cycle single phase AC welding transformers, each rated for 1000 amperes output at 40 load volts, were installed in a parallel arrangement.

As will be seen from a subsequent discussion of operation with AC power, it was found possible to melt very successfully all tantalum alloys selected for the scale-up operation. In addition, several pure tungsten electrodes of 5/8" and 1" diameter were melted satisfactorily, as was one W-5% Re alloy. Before proceeding with this presentation, however, digression must be made to describe an intermediate screening technique which was devised at a time when difficulty was being encountered with pilot ingot production.

The originally outlined procedure of alloy screening and scale-up involved the manufacture of 20-gram alloy buttons which were subjected to various metallurgical tests. On the basis of test results, the better alloys were to be scaled-up directly to a 2" diameter ingot produced by consumable electrode arc melting. Since considerable trouble was being encountered in developing ingot melting practices, it was felt necessary to employ an intermediate procedure whereby a cast structure could be subjected to some type of fabrication study. The size of the melt was to be somewhere between the 20 gram buttons, which were too small, and the 6 lb. ingots, which could not be produced as desired. A compromise melt size of 150 grams was selected since this could be handled with the existing button furnace facility described in Appendix A. A special shape copper mold was designed to form rectangular slabs or sheet-bars of the alloys melted, dimensions being approximately 3" x 1-1/4" x 1/2" thickness. These slabs were then surface conditioned, canned in stainless steel pipe for oxidation protection, and rolled to .100" thick strip at 1200°C.

This procedure had been used previously for the production of a Ta-7.5W-5Hf-0.1C alloy into strip for testing. A single test specimen had resulted whose 2200°F properties were sufficiently interesting to attempt further testing. The results of this early test were as follows: Ultimate tensile strength - 82,000 psi, 0.2% yield strength - 66,000 psi, total elongation - 9.8%. (These results are quite close to those obtained later on a Ta-6W-6Hf alloy.)

Thirteen more slabs were prepared and processed in this manner. The compositions were as follows:

Ta-2Mo-2V	Pure Ta
Ta-2W-2V	Ta-2W-2Hf
Ta-4Mo-4Hf	Ta-8W-8Hf
Ta-4Mo-4V	W-8Re
Ta-4W-4V	Ta-4Zr
Pure Ta	Ta-8Zr
Pure Ta	

Most of the alloys required about 600 amperes and were double melted. They were given a grinding treatment to produce flat top and bottom surfaces but

no edge conditioning was performed. Two slabs, one pure Ta and one Ta-10W, were used to evaluate glass as a protective coating. The remaining alloys, including slabs of Ta and Ta-10W, were canned in stainless steel packs before rolling. The Ta-10W alloy had previously been produced as an extruded sheet bar from a 5-lb arc melted ingot. This had been the only successful DC vacuum arc melt, followed by hot extrusion, that had been made at this stage of the program. An alcohol base glass slurry was applied to the uncanned slabs before heating, prior to hot rolling. After each rolling pass, the coating was conditioned by dipping in glass powder.

The alloys were rolled on a two-high 8" x 8" Stanat mill. The slabs were heated in a gas fired furnace to 1250°C and held at temperature for 15 minutes. The furnace was continuously purged with argon. The material was heated five minutes at 1250°C between passes to maintain temperature. Rolling was terminated when pack thickness was reduced sufficiently to produce .100" thick sheet, or when excessive cracking occurred. Approximately 15% reduction was taken each pass. The results of these rolling experiments are presented in Table XII.

Comparison of the canned and coated Ta and Ta-10W alloys after rolling indicates that glass offers no protection from contamination. Cross-sectional Tukon hardness traverses showed appreciable edge hardening (oxygen penetration) for the glass coated alloys and essentially no hardness change for the canned alloys. Due consideration was given to the expected variation in hardness across the worked section. The canned Ta and Ta-10W slabs rolled well without can failure and cracking. The glass coated specimens cracked transversely. The cracks propagated from the edge, 45° to the rolling direction, across the banded grains.

The fabricability of the alloys using the techniques outlined above was generally poor. It must be emphasized, however, that working was done under the most undesirable conditions, mainly biaxial stressing of as-cast slabs having undulating surfaces. In addition to unfavorable structure and stress distribution during working, one or more of the following undoubtedly affected workability:

TABLE XII

RESULTS OF CAST SHEET BAR ROLLING AT 1250°C

Alloy	Protective Coating	Number of Passes	Microstructure	Remarks
Ta	Stainless Steel	8	Banded	No cracks. Orange peel surface.
Ta-4Mo-4V	"	9	Heavily banded. Intergranular and transgranular cracks.	Can broke. Longitudinal and edge splits.
Ta-4W-4V	"	9	Heavily banded. Intergranular cracks.	Can broke.
Ta-8Re	"	8	Banded. Transgranular and intergranular cracks.	Can broke. Specimen full of cracks and splits.
Ta-4Hf	"	9	Banded. Intergranular cracks.	Can broke. Specimen broke up completely.
Ta-8Hf	"	8	Banded. Intergranular cracks.	Can broke. Longitudinal and transverse splits.
Ta-2W-2Hf	"	8	Banded	No cracks. Orange peel surface
Ta-8W-8Hf	"	8	Banded. Intergranular cracks	Can broke. Specimen crumbled.
Ta-4Mo-4Hf	"	8	Intergranular cracks.	Can broke. Edge splits. Longitudinal and transverse cracks.
Ta-4Zr	"	8	Banded. Intergranular cracks.	Can broke. Specimen crumbled.
Ta-8Zr	"	7	Banded	Can broke. Longitudinal and edge splits.
Ta-2Mo-2Zr	"	9	Banded. Intergranular cracks	Can broke. Large transverse splits.
Ta-2W-2Zr	"	8	Banded. Intergranular cracks	Can broke. Split in longitudinal direction.

TABLE XII (Cont'd)

Alloy	Protective Coating	Number of Passes	Microstructure	Remarks
Ta	Stainless Steel	7	Banded. No cracks.	No surface cracks. Orange peel surface. Hardness traverse indicated no contamination.
Ta	Glass	5	Banded. Cracks extending into specimen from edges.	Surface heavily eroded. Base metal hardness greatly increased. Apparent reaction with glass.
Ta-10W	Stainless Steel	7	Banded. No cracks.	No surface cracks.
Ta-10W	Glass	5	Banded. Cracks extending into specimen from edges.	Surface heavily eroded. Base metal hardness greatly increased. Apparent reaction with glass.

(1) Can failure and resulting oxygen penetration leading to the formation of a low melting oxide.

(2) Possible penetration of Ni, Cr and Fe (from the stainless steel can) leading to general grain boundary embrittlement by the formation of a brittle phase or low melting eutectic.

(3) Grain boundary weakness at the rolling temperature.

Without an extensive study of each alloy it was impossible to determine the cause of failure in each case.

Upon conclusion of the intermediate screening study, the alloy scale-up work was resumed. A total of twelve alloys were chosen for scale-up development, using the previously described improved processing methods. Most of these alloys were different from the ones used in the earlier scale-up attempts. Pure Ta and W were processed concurrently to furnish a basis for comparison in consolidation, fabrication and testing. The compositions selected were as follows:

Pure Ta	Ta-4Hf-4Cb
Pure W	Ta-4Hf-4Mo
Ta-2W-2Hf	Ta-4Cb-4Mo
Ta-2W-2Re	Ta-4Mo-4Re
Ta-8W-4Hf	Ta-4Zr
Ta-2W-4Hf	Ta-8Zr
Ta-8W-2Hf	W-5Re

The preponderance of alloys in the Ta-W-Hf system is due to the fact that alloys in this system up to 8% W or 8% Hf possessed good hardness, reasonable ductility and were predominantly single phase. Also, the flatness of slope of the hardness curves to at least 1200°C was an encouraging indication of strength retention at elevated temperatures. The Ta-2W-2Re alloy was chosen because of a combination of excellent melting characteristics, good fabricability and ease of machining. The Ta-4Hf-4Cb and Ta-4Hf-4Mo alloys were selected to substitute Mo and Cb for W, thus furnishing a comparison of strengthening effects. The Ta-4Cb-4Mo alloy was arbitrarily picked to provide a solid solution alloy containing neither W, Re or Hf. The Ta-4Mo-4Re alloy

was included to provide information on the effects of Re on a Mo-bearing ternary alloy as an analogy to the Ta-W-Re system. The Ta-4Zr and Ta-8Zr alloys were provided as experimental selections because these compositions appeared to be amenable to heat treatment, based on information obtained from the screening studies. The W-5 Re alloy was selected because of the interesting effect of small rhenium additions in reducing the hardness of tungsten.

The improved electrode preparation procedure previously described was used in the manufacture of tantalum electrode bars. A total of thirteen bars were pressed at 50 tons/in^2 and heated in a .01 micron vacuum to 1600°C, being held for one hour at temperature. Bars were argon arc welded individually to columbium adapters so that maximum melt yield could be realized. Pure tungsten electrodes were purchased as 5/8" diameter sintered and swaged bars and melted directly. Most of this melting was performed using AC power. The W-5 Re alloy was prepared using a rhenium wire forced into a slot in a swaged tungsten bar. The proper conditions for AC melting of tungsten and tantalum were quickly established, and the results were very satisfactory. Ingots were uniformly sound, although melted but once. The thin "skull" or shell surrounding the ingot, typical of AC melts, could be removed readily. Furnace heating and electrode overheating were not encountered. Arc stability was excellent and no damage was inflicted on crucible or furnace components during the entire series of runs. Total power consumption for AC melting was considerably less than that required for DC melting of similar alloys. In view of the results obtained, it appears that AC melting is the preferred manner of producing tantalum and tungsten alloy ingots, at least in the small sizes considered during this study. The results of all of the melting experiments are contained in Tables XIII and XIV. It was found possible to condition all tantalum base alloy ingots by lathe-turning using single point high speed steel tools. In most cases, the removal of 1/8 inch from the diameters of the cast ingots was sufficient to produce a smooth surface free of folds or pits and suitable for extrusion. The bottoms of the ingots were faced off by turning after the botto

TABLE XIII

MELTING PARAMETERS OF TA-BASE ALLOYS

Composition wt.%	Power	Voltage volts	Current amps	Vacuum microns	Melt Time seconds	Melt Rate lbs/min	Remarks *
Ta-10W	DC	30	2900	1	318	.8	Fair surface
Ta-2W-2Hf	DC	32	3300	-	363	.5	Small ingot from short electrode.
Ta-10Hf	DC	32	3300	-	-	-	Electrode split open, DNF.
Ta-10W-10Hf	DC	32	3600	-	-	-	Partial ingot, DNF.
Ta-5W-5Hf	AC	18	2200	0.5	565	-	Poor ingot
Ta-7.5W-5Hf	DC	30	2400	0.1	60	-	Overheating and warpage, DNF.
Ta-8W-8Hf	DC	30	2700	0.1	60	-	Overheating and warpage, DNF.
Ta-8W-8Hf-0.1C	AC	20	2800	0.3	245	1.2	Satisfactory ingot.
Ta-4Hf-4W-4Re	DC	30	3200	-	85	-	Overheating, DNF.
Ta-6W-6Hf	AC	19	2800	0.5	180	1.7	Satisfactory ingot.
Ta-4W-4V	DC	27	3900	>10	310	1.2	Electrode dropped out of holder. Mold burned through.
Ta-4Hf-4V-0.1C	AC	20	2800	0.5	-	-	Electrode split, warpage, DNF
Ta-4W-4Hf-4V	DC	29	3600	1	-	-	Did not melt.
Ta	AC	25	2200	1	257	1.2	Arc gap too long. Poor ingot.
Ta	DC	31	2800	0.5	225	1.5	Mold burn-through.
Ta	DC	29	2900	1	200	1.5	Satisfactory ingot.
Ta	DC	32	2400	0.5	240	1.0	"
Ta-2W-2Re	DC	30	2400	0.5	360	0.8	"
Ta-2W-2Re	AC	20	2800	1	187	1.8	"
Ta-8W-4Hf	AC	20	2800	0.3	220	1.4	"

* DNF - Did not finish melting of electrode.

TABLE XIII (Cont'd)

Composition wt.%	Power	Voltage volts	Current amps	Vacuum microns	Melt Time seconds	Melt Rate lbs/min	Remarks
Ta-2W-4Hf	AC	20	2800	0.5	234	1.3	Satisfactory ingot.
Ta-8W-2Hf	AC	20	2800	0.4	215	1.6	"
Ta-4Hf-4Cb	AC	20	2800	0.5	230	1.4	"
Ta-4Hf-4Mo	AC	20	2800	0.3	236	1.4	"
Ta-4Cb-4Mo	AC	20	2800	/	200	1.7	"
Ta-4Mo-4Re	AC	20	2800	0.8	213	1.6	"
Ta-4Zr	AC	20	2800	0.1	201	1.6	"
Ta-8Zr	AC	20	2800	0.2	235	1.4	"

/ Vacuum Gauge Defective

TABLE XIV

MELTING PARAMETERS OF W AND A W-BASE ALLOY

Composition	Power	Amperes	Volts	Vacuum	Melt Time	Melt Rate
W	AC	1800	20	1μ	5 min.	1.0 lb/min.
W	AC	2000	25	0.2μ	4 min. 18 sec.	1.25 lb/min.
W	AC	2100	15	0.3μ	4 min. 25 sec.	0.9 lb/min.
W	AC	1800	27	0.1μ	4 min. 50 sec.	1.1 lb/min.
W-5Re	AC	1850	27	0.1μ	5 min.	1.05 lb/min.
W *	AC	3000	20	0.1μ	2 min. 30 sec.	1.9 lb/min.
W	AC	2650	25	0.1μ	2 min. 55 sec.	----

* 1" Diameter Electrode

pads had been cut off by a power hacksaw. The tops were also faced by turning until uniform cross-sections free of pipe were obtained. The two ends were machined parallel so that the finished billets were a right cylinder. A 1/16" x 30 degree bevel was machined on the top circumference of each billet to facilitate lead-in to the conical entrance of the extrusion die.

In order to enhance the probability of producing sound sheet for testing, it was decided to utilize a proven metal working technique developed for the processing of high strength columbium-base alloys. Primary breakdown of the arc cast billets was accomplished by high energy-rate extrusion, Dynapak, at the Westinghouse Materials Manufacturing Department at Blairsville, Pennsylvania. (See Appendix A) Before heating for extrusion the conditioned billets were painted with a slurry of fine glass powder (Corning 7052) and alcohol which was allowed to dry at room temperature. The billets were heated for extrusion in an induction furnace located adjacent to the Dynapak. A flowing argon atmosphere was maintained within the furnace enclosure to minimize contamination during the heating cycle. A photograph of the induction coil and enclosure is shown in Fig. 55. The billets were supported vertically within the furnace on an alumina pedestal.

Billet temperatures were measured with an optical pyrometer which was sighted through an observation port in the top of the furnace enclosure. When the billet reached extrusion temperature, the coil enclosure was removed and the billet was taken from the coil and placed in the billet container of the Dynapak. Transfer time was generally less than 5 seconds. The Dynapak was immediately fired after the billet was placed in the container. The billet was extruded through the die and caught in a barrel filled with fine dry zircon sand.

The pertinent data concerning the extrusion parameters for the tantalum-base alloys are listed in Table XV. Initial extrusion attempts were not as successful as desired due to difficulty encountered in reaching extrusion temperature. However, useful material was obtained from five of the first six extrusion attempts. The Ta-8W-8Hf alloy which contained an intentional addition of 0.1 per cent carbon broke up completely on passing through the die. The

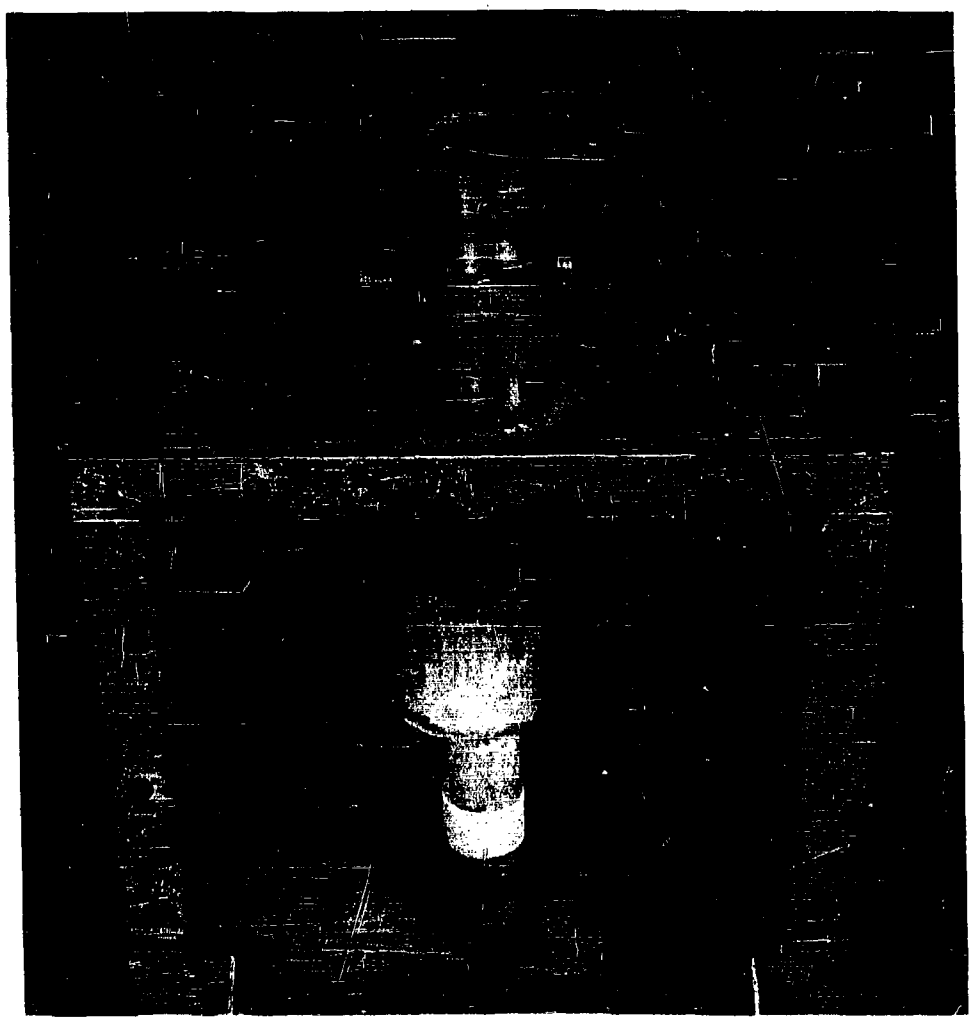

Fig. 55--Heating assembly for Dynapak extrusion

TABLE XV

DYNAPAK EXTRUSION OF TANTALUM ALLOYS[a]

Composition[b]	Billet Dimensions	Billet Weight	Billet Ends	Extrusion Direction	Extrusion Temp.	Fire Pressure	Extrusion Length	Remarks
Ta-2W-2Hf	1-3/4"x 1-7/16"	2.0 lb	Flat	Bottom First	1475°C	1000 psi	5-1/2"	Complete Extrusion-Good Surface
Ta-8W-3Hf	1-3/4"x 2-7/8"	3.8 lb	Beveled Edges	Top First	1625°C	1600 psi	Broke Up	1" of Billet Failed to Extrude - Metal Broke Up Going Through Die.
Ta-6W-5Hf	1-3/4"x 2-7/32"	3.0 lb	"	Bottom First	1485°C	1100 psi	Incomplete 4"	Partial Extrusion - Metal Alligatored Going Through Die.
Ta	1-3/4"x 2-1/2"	2.5 lb	"	Top First	1435°C	1200 psi	9"	Complete Extrusion-Excellent Surface
Ta	1-3/4"x 1-3/4"	2.4 lb	"	"	1500°C	900 psi	6"	Complete Extrusion-Excellent Surface
Ta-2W-2Re	1-3/4"x 2-7/16"	3.4 lb	Flat	"	1465°C	1400 psi	Incomplete 7-1/2"	Partial Extrusion-Poor Surface
Ta-2W-2Re	1-3/4"x 2-1/2"	3.7 lb	1/16" 30° Bevel	"	1700°C	1700 psi	8-1/2"	Complete Extrusion-Poor Surface
Ta-8W-4Hf	1-3/4"x 2"	2.9 lb	"	"	"	1600 psi	6-1/2"	Complete Extrusion-Small Nose Burst
Ta-2W-4Hf	1-3/4"x 2-1/2"	3.6 lb	"	"	"	1700 psi	7-3/4"	Complete Extrusion-Nose Burst
Ta-8W-2Hf	1-3/4"x 2-1/2"	3.8 lb	"	"	1670°C	1800 psi	8-1/2"	Complete Extrusion-Good Surface
Ta-4Hf-4Cb	1-3/4"x 2-2/4"	3.7 lb	"	"	1700°C	1800 psi	9"	Complete Extrusion-Good Surface
Ta-4Hf-4Mo	1-3/4"x 2-7/8"	3.9 lb	"	"	1700°C	1900 psi	8-1/4"	Complete Extrusion-Nose Burst
Ta-4Cb-4Mo	1-3/4"x 2-7/8"	3.9 lb	"	"	1700°C	1900 psi	9"	Complete Extrusion-Good Surface
Ta-4Mo-4Re	1-3/4"x 2-3/4"	3.9 lb	"	"	1700°C	1800 psi	Incomplete 7-1/2"	Partial Extrusion-Good Surface
Ta-4Zr	1-3/4"x 2-7/8"	3.9 lb	"	"	1700°C	1860 psi	7-3/4"	Complete Extrusion-Nose Burst
Ta-8Zr	1-3/4"x 3-1/8"	3.6 lb	"	"	1700°C	2000 psi	Broke Up	Billet Disintegrated to Small Pieces

(a) 4:1 Reduction Ratio-Sheet Bar Die
Corning 7052 Glass in Container and on Die Face for Lubrication
Total Stroke - 12.5 inches
Total Weight of Ram Assembly - 1686 lbs.
Total Weight of Sub Assembly - 8803 lbs.

(b) Weight Percent

failure of this alloy to extrude may have been due to the low extrusion temperature combined with the possible adverse effect of the carbon additions on the flow characteristics of the alloy. Resolution of the heating problem enabled the extrusion of the 10 remaining billets at 1700°C. Of these, 8 extruded completely with a high yield of usable material, one jammed after extruding 70% of the total volume, and one disintegrated into small pieces.

The failure of the Ta-8Zr billet to extrude was probably due to the incompatability of the alloy with the extrusion process rather than a failure of the extrusion technique.

Because the extruded bars were exposed to the atmosphere during cooling from extrusion temperature, it was necessary to condition the sheet bars prior to additional work. The conditioning of the sheet bars included removal of the front and back ends to sound metal. The operation was done with an abrasive cut-off wheel. The top, bottom and side surfaces were machined on a shaper to remove 0.020 to 0.030 inch of material from all sides. High speed steel tools were used on the shaper. This operation removed all scale and the contaminated layer underneath. Each slab was then hand ground to remove all sharp corners and edges to minimize the possibilities of crack formation during the subsequent rolling operation. Finally, the bars were etched in an acid solution to remove smeared metal and reveal any small cracks. If cracks were found, they were removed by spot grinding.

Prior to rolling, the conditioned extruded sheet bars were encased in flattened stainless steel pipes to protect the tantalum-base alloys from oxidation during rolling. Longitudinal stainless steel bars were inserted along the sides of the slabs to furnish some side restraint during rolling with the object of reducing slab edge cracking. Alumina powder in an alcohol slurry was generously applied to the slab and inner surface of the pack to prevent welding of the two metals during rolling. The slab and the restraint bars were inserted into the flattened stainless steel pipe, and the ends were crimped together for welding. A nipple was inserted and welded into one end to facilitate evacuation. After pumping to the low micron range, argon was admitted to backfill the pack. The nipple was then pinched off and welded to complete the seal.

Rolling was done at 1250°C on a two-high laboratory reversing mill. (See Appendix A) Reductions were made at 0.050 inch per pass with reheats to 1250°C between each pass. This procedure was followed until the packs attained a thickness of 0.200". The final two reductions were made without an intermediate reheat to impart some degree of low temperature work to the material. After rolling was completed the stainless steel cases were removed from the strips. Figures 56-60 show typical results of each fabrication step.

Rough test specimens were cut from the strip with a band saw and were subsequently finish-machined to size and surface ground on top and bottom to produce the required 0.050" test specimen thickness. Since the rolled thickness was generally 0.090" to 0.100", at least 0.020" was ground from each surface, thus removing any existing surface contamination. The effectiveness of these conditioning procedures was checked by means of cross-sectional microhardness traverses of the material at each stage of processing. The results of these tests demonstrated that sufficient surface metal was removed in all cases to produce uniform hardnesses across the entire section.

Two attempts to fabricate the W-5Re alloy have been made. Ammonium paratungstate and ammonium perrhenate were coprecipitated as the oxides, using the procedures usual for the production of tungstic acid. The resulting powder was then hydrogen reduced, and the metallic powder was consolidated to a bar for direct resistance sintering. The alloy was then sintered and attempts were made to swage the sintered bar into rod for testing. Considerable difficulty was encountered even at 1700°C because of the extremely rapid increase in hardness due to working. A rod 1/4 inch in diameter was finally produced. Metallographic examination showed numerous microcracks in the structure. These cracks were not associated with the difficulty in working, but rather were due to contamination of the alloy by oxygen. Even the low percentage of rhenium in this alloy reacted with oxygen to form a liquid oxide penetrating the grain boundaries. This difficulty has been previously reported for pure Re and for the W-30 Re alloy. Samples for compression testing of this alloy have been made but not yet tested. A W-5Re alloy was

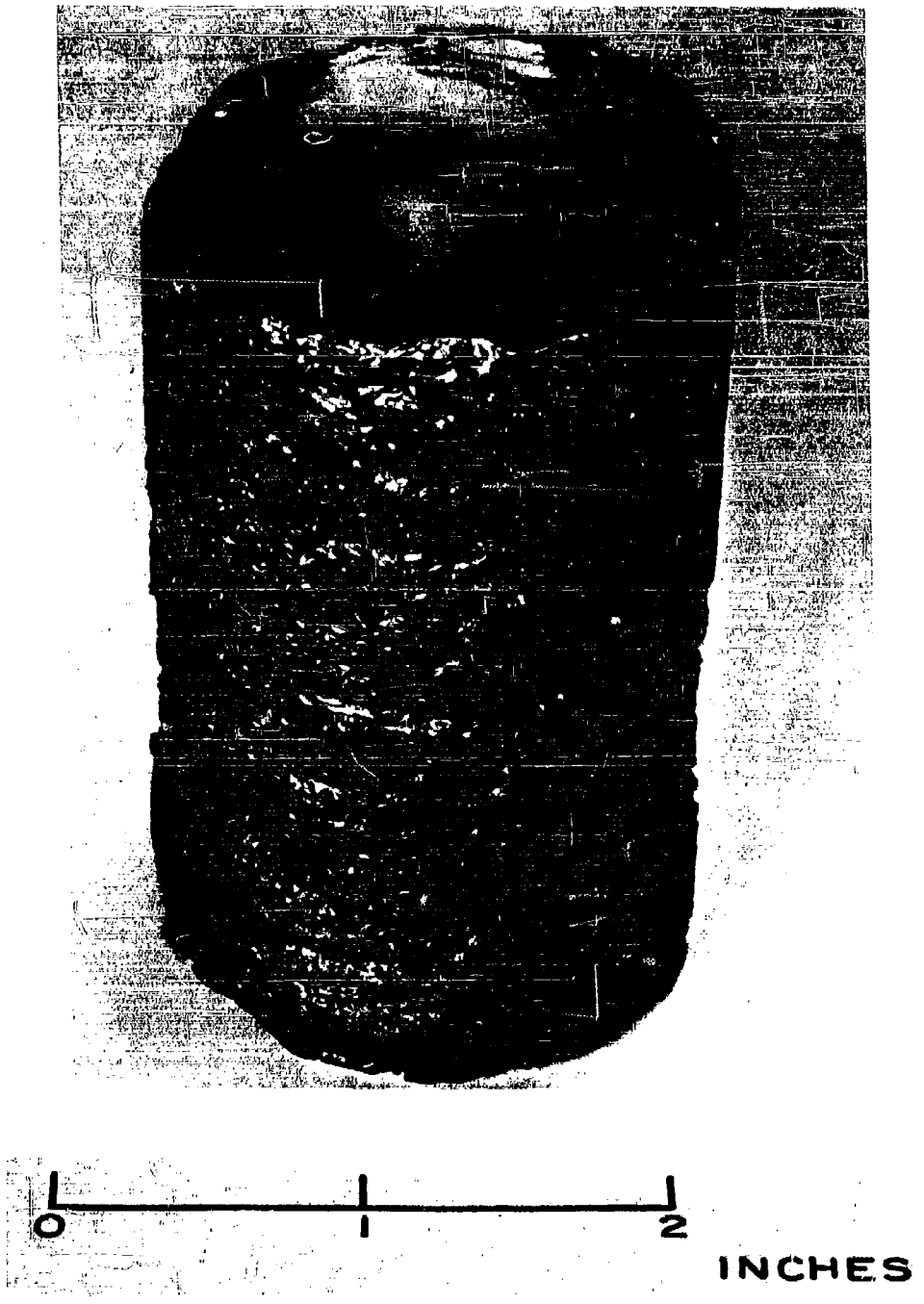

Fig. 56--Tantalum Ingot As Arc Melted (AC Power)

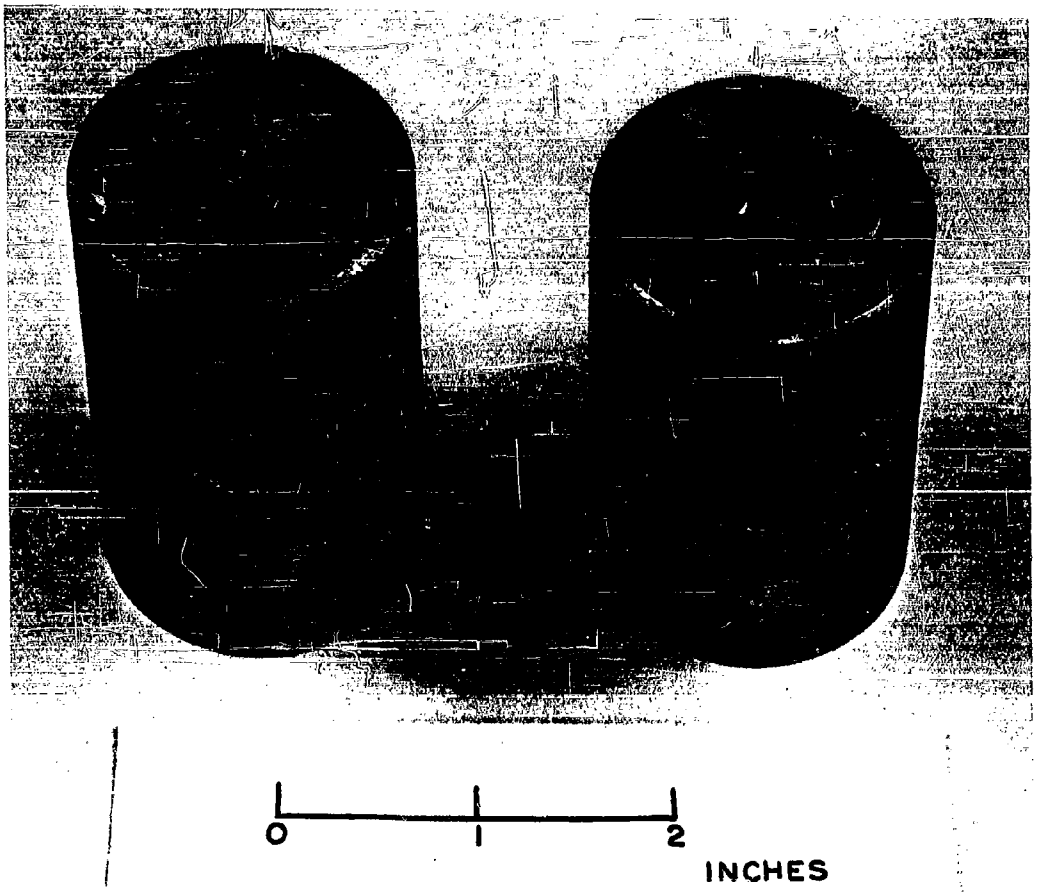

Fig. 57--Conditioned Tantalum Ingots

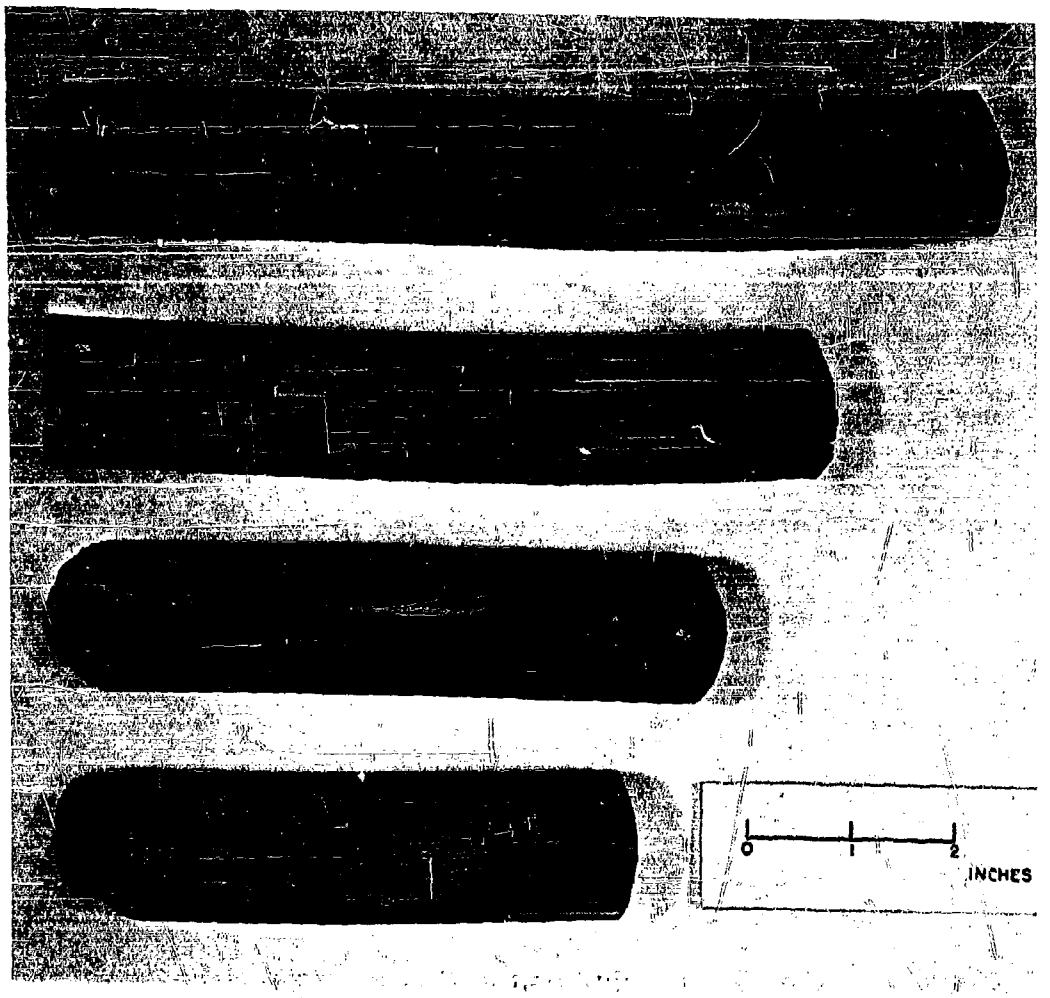

Fig. 58--Tantalum Sheet Bar Extrusions

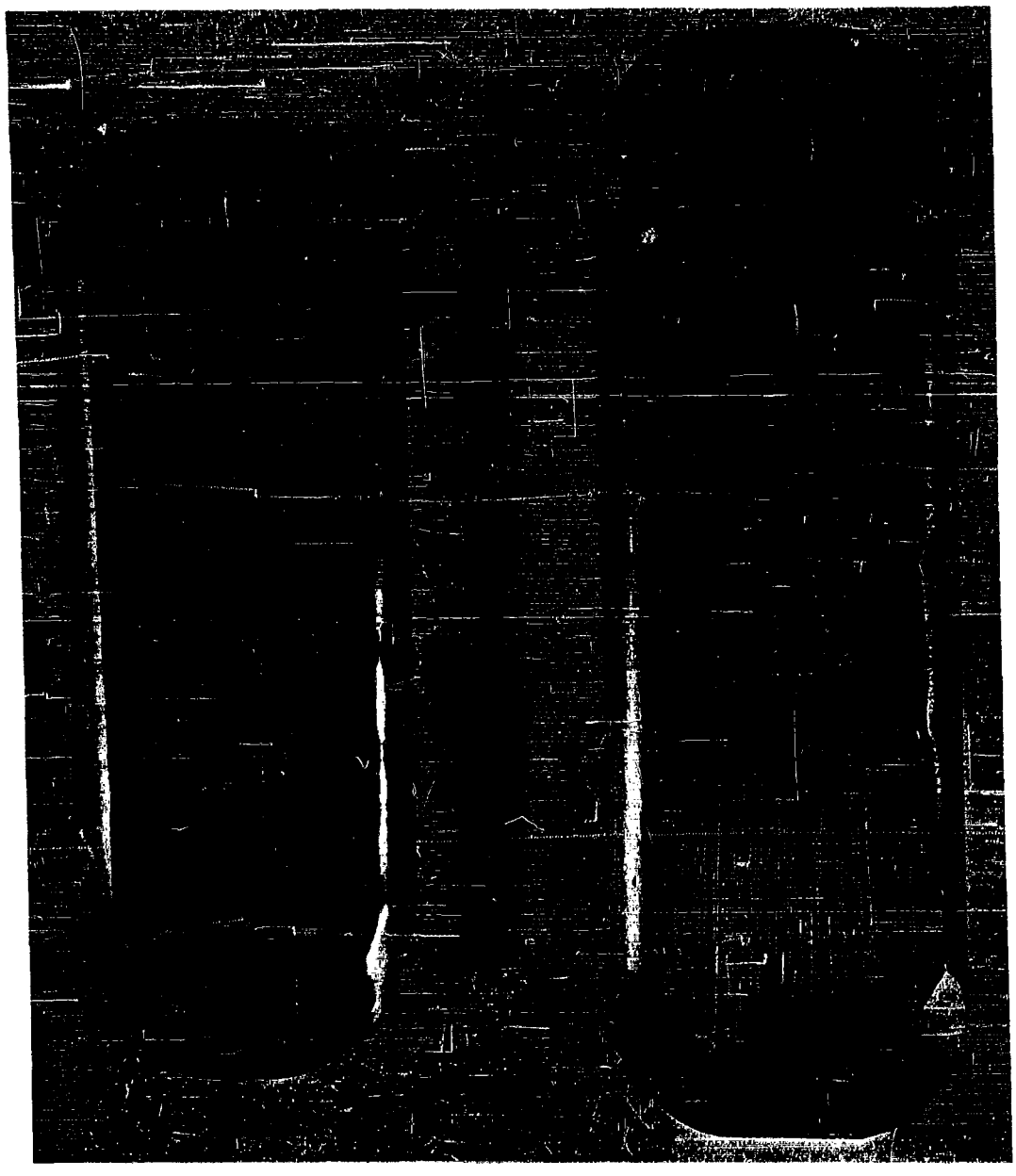

Fig. 59--Conditioned Tantalum Sheet Bar Extrusions

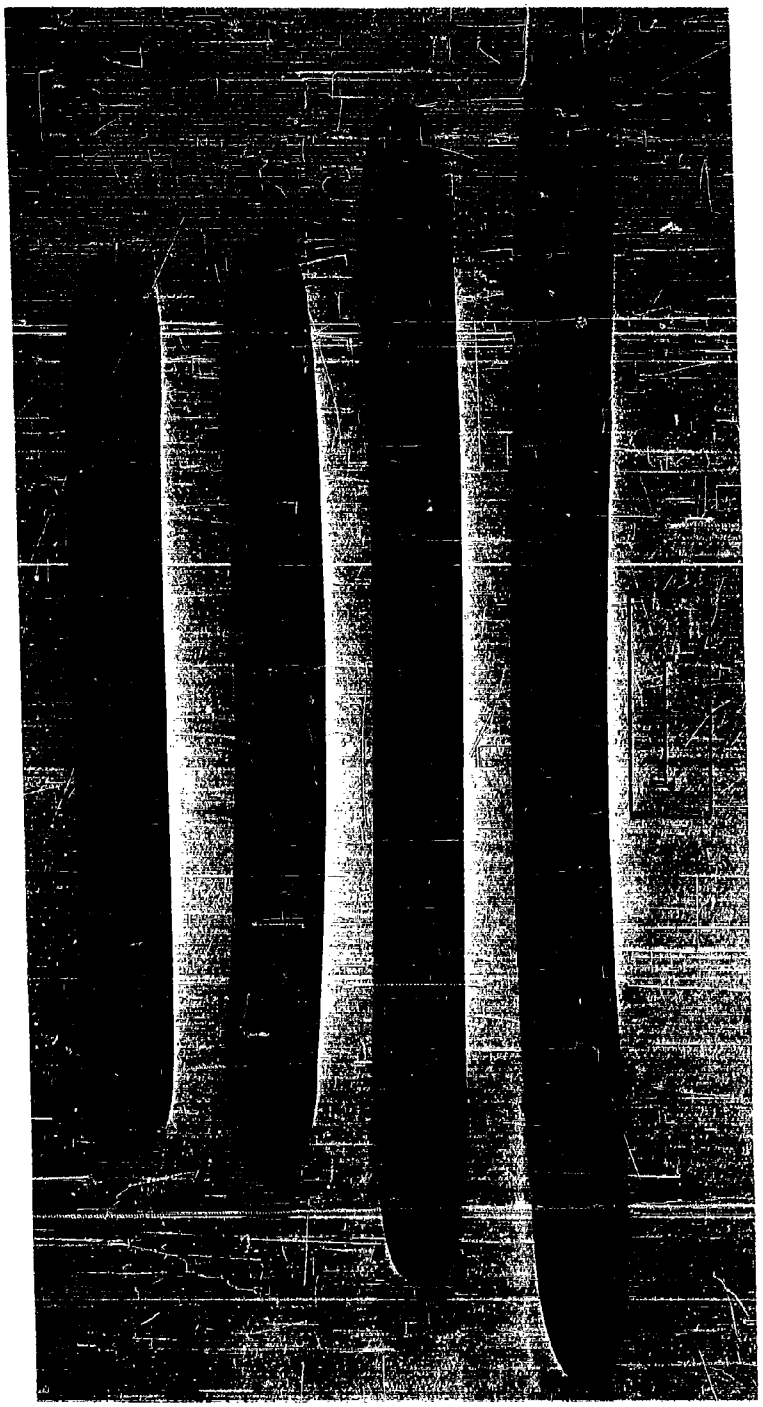

Fig. 60--Tantalum Alloy Strips

also made by arc melting as discussed previously. This alloy is scheduled to be Dynapak extruded in the immediate future and will be worked further if possible.

E. MECHANICAL TESTING -- Wrought strip specimens of the various alloys were stress relieved at 1100°C for 1 hour and then subjected to tensile tests at temperatures ranging from -320°F (liquid nitrogen) to 2700°F. The low temperature tests were carried out on a standard tensile machine modified with a low temperature chamber surrounding the specimen, grips, and extension rods, and through which liquid nitrogen was continuously circulated. With a special valving arrangement it was possible to maintain a constant temperature between ambient and -320°F by regulating the flow of the liquid nitrogen. Elevated temperature tests were conducted in high vacuum in radiant resistance heated furnaces. The strain rate used for all tests was 360% per hour. Hardness measurements were taken on the specimens before and after exposure to help determine whether recrystallization or contamination, or both, had occurred. Supplementing this, cross section Tukon hardness traverses were made to furnish a positive check on contamination, and micros were examined to detect any recrystallization during test. No evidence of contamination was found in any of the specimens tested. Partial or full recrystallization occurred in some compositions when tested at 2500°F.

The results of these tests are contained in Table XVI. None of the alloys was brittle at liquid nitrogen temperatures as evidenced by the retention of significant elongation (8-21%) and high reduction in area values (38-62%). These values are approximately equivalent to those obtained with pure tantalum. The Ta-W-Hf alloys as a group displayed higher strengths at elevated temperatures than the other alloys. The alloys Ta-2W-4Hf, Ta-6W-6Hf, Ta-8W-2Hf and Ta-8W-4Hf exhibited outstanding strengths at 2200° and 2500°F. When compared with existing high strength alloys of molybdenum and columbium which have been processed in a similar manner, these tantalum alloys exhibit marked superiority on a direct strength basis. If a strength-weight comparison is made on the basis of alloy densities, these particular alloys are still very attractive at the higher

TABLE XVI

RESULTS OF TENSILE TESTING ON TANTALUM BASE ALLOYS

95% Reduction, Stress Relieved 1 Hour at 2000°F

Composition wt.%	Testing Temperature °F	Ultimate Tensile Strength psi	0.2% Yield Strength psi	% Elongation	% Reduction in Area
Pure Ta	-320	162,000	162,000	5	54
	-100	109,000	109,000	21	74
	75	88,000	87,000	19	71
	300	79,000	70,000	15	~100
	500	94,000	77,000	13	~100
	1000	81,000	65,000	13	40
	1500	63,000	60,000	15	~100
	2200	17,800	15,000	32	75
	2500	6,000	3,800	>61	--
Ta-2W-2Hf	-100	121,000	113,000	15	73
	75	110,000	105,000	16	64
	2200	52,000	48,000	16	41
	2500	24,800	20,700	37	65
	2700	16,400	14,400	51	~100
Ta-2W-4Hf	-320	156,000	153,000	21	60
	-100	124,000	118,000	16	65
	75	113,000	106,000	16	65
	2200	76,000	72,000	15	40
	2500	27,600	24,500	65	~100
	2700	20,500	19,500	106	~100
Ta-8W-2Hf	-320	190,000	184,000	18	44
	-100	150,000	146,000	17	64
	75	135,000	130,000	15	60
	2200	85,000	78,000	15	28
	2500	54,000	38,800	26	47
	2700	29,000	23,700	64	81
Ta-8W-4Hf	-320	205,000	204,000	11	16
	75	147,000	140,000	15	50
	2200	91,000	80,000	23	37
	2500	43,000	37,700	50	74
	2700	32,200	30,300	67	73

TABLE XVI (Cont'd)

Composition wt.%	Testing Temperature °F	Ultimate Tensile Strength psi	0.2% Yield Strength psi	% Elongation	% Reduction in Area
Ta-6W-6Hf *	2200	78,000	65,000	15	33
	2500	50,000	44,000	15	26
Ta-10W	75	81,000	78,000	10	83
	2200	38,600	37,500	12	~100
Ta-4Mo-4Hf	-320	199,000	197,000	16	38
	-100	155,000	151,000	16	48
	75	144,000	139,000	16	60
	2200	85,000	78,000	26	47
	2500	39,600	35,200	59	76
	2700	28,700	28,200	79	84
Ta-4Cb-4Hf	-320	142,000	139,000	19	56
	-100	115,000	107,000	16	66
	75	104,000	97,000	17	54
	2200	68,000	62,000	16	42
	2500	23,700	21,200	88	~100
	2700	18,700	18,600	90	~100
Ta-4Cb-4Mo	-320	190,000	190,000	11	62
	-100	144,000	144,000	20	71
	75	122,000	122,000	15	66
	2200	54,000	48,000	17	48
	2500	19,800	18,700	48	51
	2700	16,700	16,000	11	95
Ta-2W-2Re DC Melted	-320	192,000	190,000	6	52
	-100	147,000	147,000	17	81
	75	128,000	127,000	18	77
	2200	55,000	43,000	15	42
	2500	21,600	17,400	44	56
Duplicate	2700	15,900	14,700	45	40
Tests	2700	16,700	15,700	48	48
	3000	12,900	9,600	49	67
Ta-2W-2Re AC Melted	-320	190,000	188,000	8	56
	-150	147,000	147,000	22	71
	75	123,000	123,000	18	74
	2200	57,000	51,000	14	56
	2500	27,300	23,400	24	55
	2700	15,200	13,600	54	67

* Tested in the as-extruded and stress relieved condition.

temperatures. The Ta-2W-2Hf alloy of this series is of lower strength but still may be considered a very interesting alloy since it has desirable melting characteristics and demonstrates excellent fabricability, in addition to possessing a satisfactory high temperature strength. The other alloys consisting of W-Re, Hf-Mo, Cb-Mo, Hf-Cb and W additions to a tantalum base are likewise of interest. There is also present in these alloys a combination of high temperature strength and low temperature ductility which might be potentially useful. The Ta-4Hf-4Mo in particular possesses exceptionally high strength at 2200°F and 2500°F, combined with the usual high ductility at -320°F. The Ta-2W-2Re is capable of being melted with either DC or AC power, an unusual feature, since most of the other tantalum alloys could be melted only with AC power. This particular alloy had unusually good melting characteristics and was easily fabricated to strip with excellent surface quality. The Ta-4Hf-4Cb and Ta-4Cb-4Mo alloys exhibited intermediate high temperature strengths which were considerably higher than Ta-10W or the common molybdenum or columbium alloys.

In summary, on the basis of the initial tests conducted on wrought stress-relieved material it appears that certain useful tantalum alloys can be developed that will possess excellent mechanical properties in the temperature range 2000-3000°F. Furthermore, with the high degree of low temperature ductility inherent in these materials it would seem that such alloys will be formable and weldable.

IV. DISCUSSION OF RESULTS

A. TANTALUM BASE ALLOYS -- Throughout this investigation, the assumption was made that the hardness of an alloy both at room temperatures and at elevated temperatures could be closely correlated with the short time tensile properties. In general, the results obtained have tended to support this assumption. Fig. 61 shows the relationship between hardness and 0.2% yield stress at room temperature for several alloys. Due to equipment difficulties, few hardness points were obtained at 2200°F so a direct comparison of hardness and strength at elevated temperature could not be made. However, if hardness at 2000°F is plotted against yield strength at 2200°F, a simple linear relationship is found (Fig. 62). These results indicate that comments regarding the changes in hardness of Ta-base alloys can be generalized to include changes in strength with some degree of confidence.

At room temperature the alloying elements V, Mo, Re, Zr, Hf, W, and Ti increase the hardness of Ta. The elements are listed in order of decreasing effectiveness, evaluated as binary additions at a level of less than 5% by weight. At a 10% level, the order of effectiveness is Re, V, Mo, Zr, W, Hf, and Ti. When ternary additions are made, Zr and Hf are extremely effective hardeners. Due to the poor fabricability of Ta alloys containing 4% Zr or more, only a small amount of Zr can be added. When the hardness at elevated temperatures is considered, again the addition of Hf yields outstanding properties. This conclusion is also borne out by the tensile results at elevated temperatures. If the percent of low temperature hardness retained at high temperature* is examined, a curious fact becomes evident. The addition of about 4% Hf results in an alloy which maintains the maximum amount of its low temperature hardness. The addition of W to this 4% Hf alloy results in a very slight decrease in the HRF until a level of between 8 and 16% W is reached, when a sharp drop is found. Figure 63 shows this behavior clearly. If the actual hardness values are considered, the peak is in the neighborhood of the Ta-8W-4Hf composition

* Previously defined as the HRF.

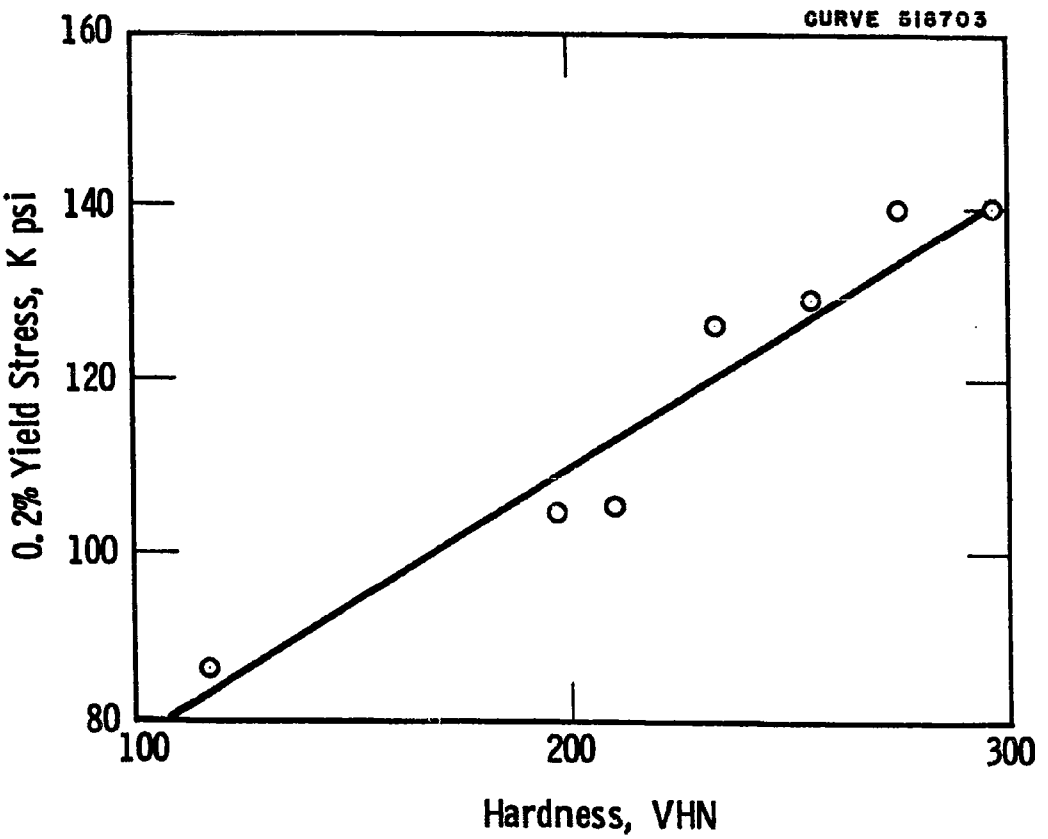

Fig. 61--Yield stress as a function of hardness at room temperature

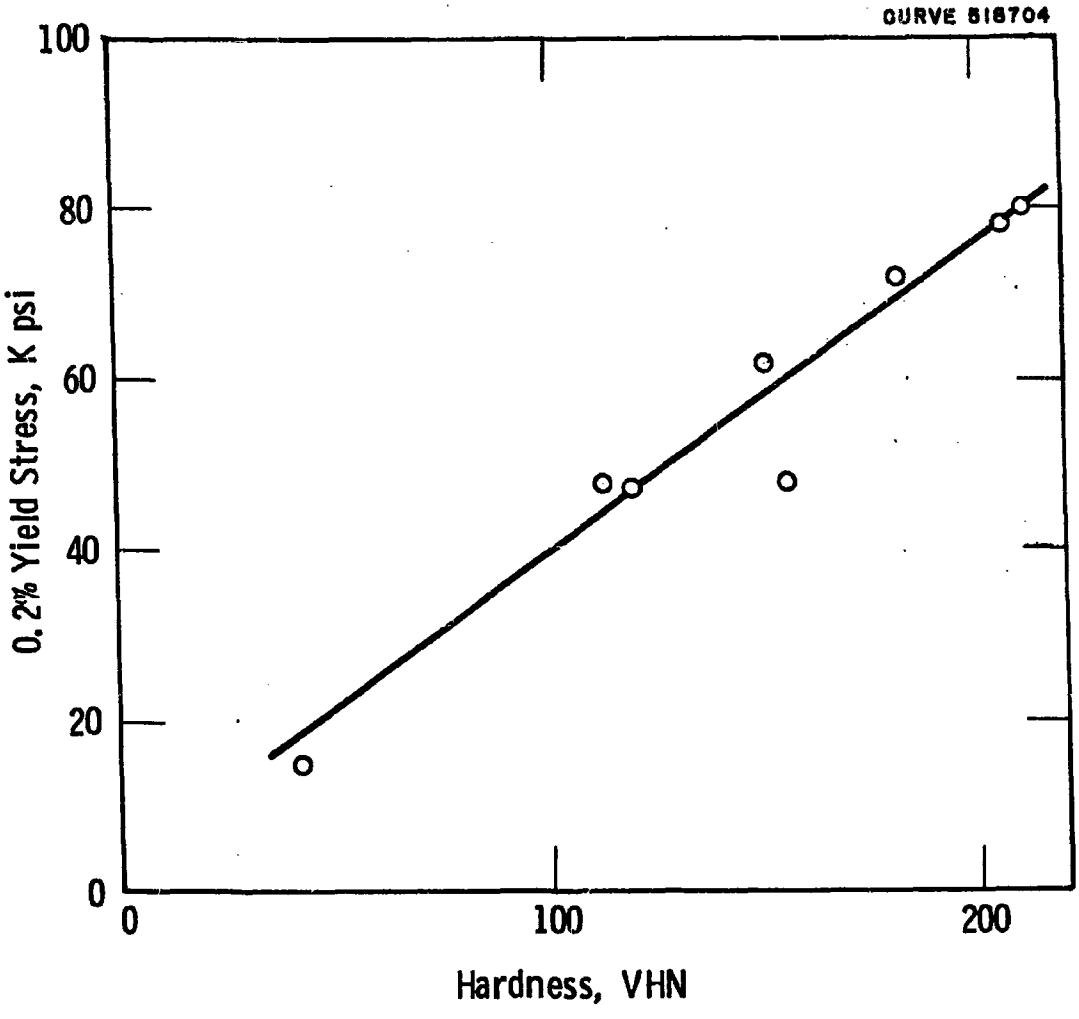

Fig. 62--Yield stress at 2200°F as a function of hardness at 2000°F

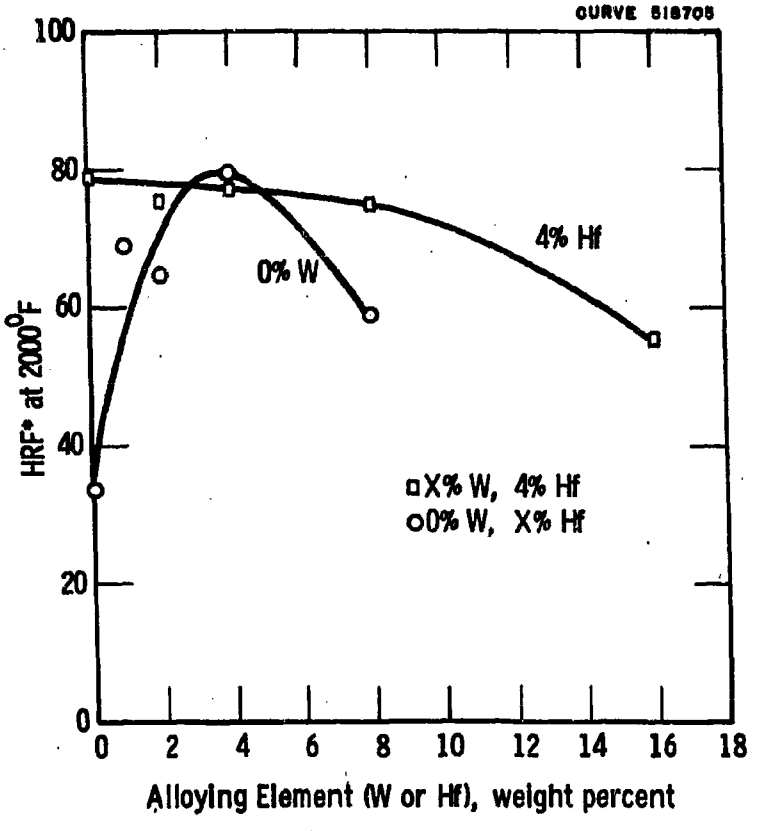

Fig. 63--Hardness retention of Tantalum base alloys as a function of Hf and W content

$$*\text{HRF} = \frac{\text{VHN at Temp.}}{\text{VHN at R. T.}} \times 100$$

Examination of the microstructures of the Ta-W-Hf alloys revealed a small amount of a second phase, whereas no such phase was found in the Ta-W alloys. The exact nature of this phase has not yet been determined, but it is almost certainly a precipitate formed by reaction of the Hf with interstitial impurities. If this is so, then the peak in HRF would probably be associated with the critical Hf content necessary to produce the optimum dispersion of the precipitated phase. This critical level would, of course, be a function of the exact interstitial content of the alloy. It is also probable that the interstitial level present in the particular alloys studied is not the optimum value, so that further improvement can be made by further investigation.

Another criterion of the utility of an alloy is the ability of the alloy to be made into a useful shape. The fabricability of alloys of Ta was studied by both cold rolling and 1200°C forging. While the testing conditions were relatively severe, it was felt that if a button could be worked by these methods, then a larger ingot could be worked by more sophisticated techniques. This indeed turned out to be true, since all alloys except two that were chosen for further studies were successfully fabricated in the scale-up program.

Examination of the data on workability and on room temperature hardness revealed a rough correlation between the limit of fabricability and a hardness of 300 VHN. This "rule of thumb" was used extensively throughout this work. It is probable that a level of 350 VHN could be used and workability would still be good.

The oxidation resistance of all alloys studied was quite poor. The best alloy found in the Ta-rich alloys was the Ta-8W-8Hf alloy, in which the oxidation rate at 1200°C was about 1/4 that of pure Ta. Oxidation resistance was not used as a criterion for selection of alloys for scale-up studies.

Based upon the limit of 300 VHN for workable alloys and the good hot hardness of the 4% Hf alloys, an optimum composition for an alloy to be scaled up could be predicted. The alloy, Ta-8W-4Hf, would have a room temperature hardness of about 275, a 2000°F hardness of about 210, reasonable workability and low temperature ductility, and an oxidation rate of about 1/2 that of pure

Ta. A number of alloys were made at and near this composition. A number of alloys were also made to check the effect of substituting other elements for W.

The Ta-W-Hf system was not the only system that appeared of interest. The rapid increase in hardness caused by the addition of Re and the relatively good retention of this hardness at elevated temperature indicate that this system should also be examined further. Only 2 alloys were made using the additions, the Ta-2W-2Re and Ta-4Mo-4Re. The Ta-2W-2Re was expected to be quite workable and to have a relatively low strength at elevated temperature. The Ta-4Mo-4Re was expected to have marginal workability and a high strength at elevated temperatures. A Ta-4Mo-4Cb alloy was made to check the properties of an alloy containing neither W, Hf, nor Re. This alloy was expected to be moderately workable but having a low strength level.

In general, the high temperature properties met expectations in all respects. Most of the alloys were also tested at low temperatures where they were found to possess very attractive ductilities, even at liquid nitrogen temperatures. Figures 64 and 65 show the 0.2% yield stress of these alloys as a function of temperature. Almost all of the alloys tested had an unexplained minimum value of reduction in area at 2200°F. All alloys were at least partially recrystallized during testing at 2500°F, except the Ta-8W-4Hf alloy which showed partial recrystallization after testing at 2700°F.

Since testing at 2500°F was above the dynamic recrystallization temperature, the sharp drop of properties between 2200°F and 2500°F is not unusual. The rather good properties found at 2700°F, well above the recrystallization temperature for most of the alloys, indicate that appreciable strength will still be found at 3000°F. This conclusion is confirmed by the one test made at this temperature.

The alloys can generally be separated into two classes, the "high strength" alloys (including Ta-8W-2Hf, Ta-8W-4Hf, Ta-6W-6Hf, and Ta-4Mo-4Hf) and the "moderate strength" alloys (including Ta-2W-2Hf, Ta-2W-4Hf, Ta-4Cb-4Hf, Ta-2W-2Re, and Ta-4Cb-4Mo). The low temperature ductility of all of these alloys is excellent, as was shown in Table XVI. The equivalence in properties

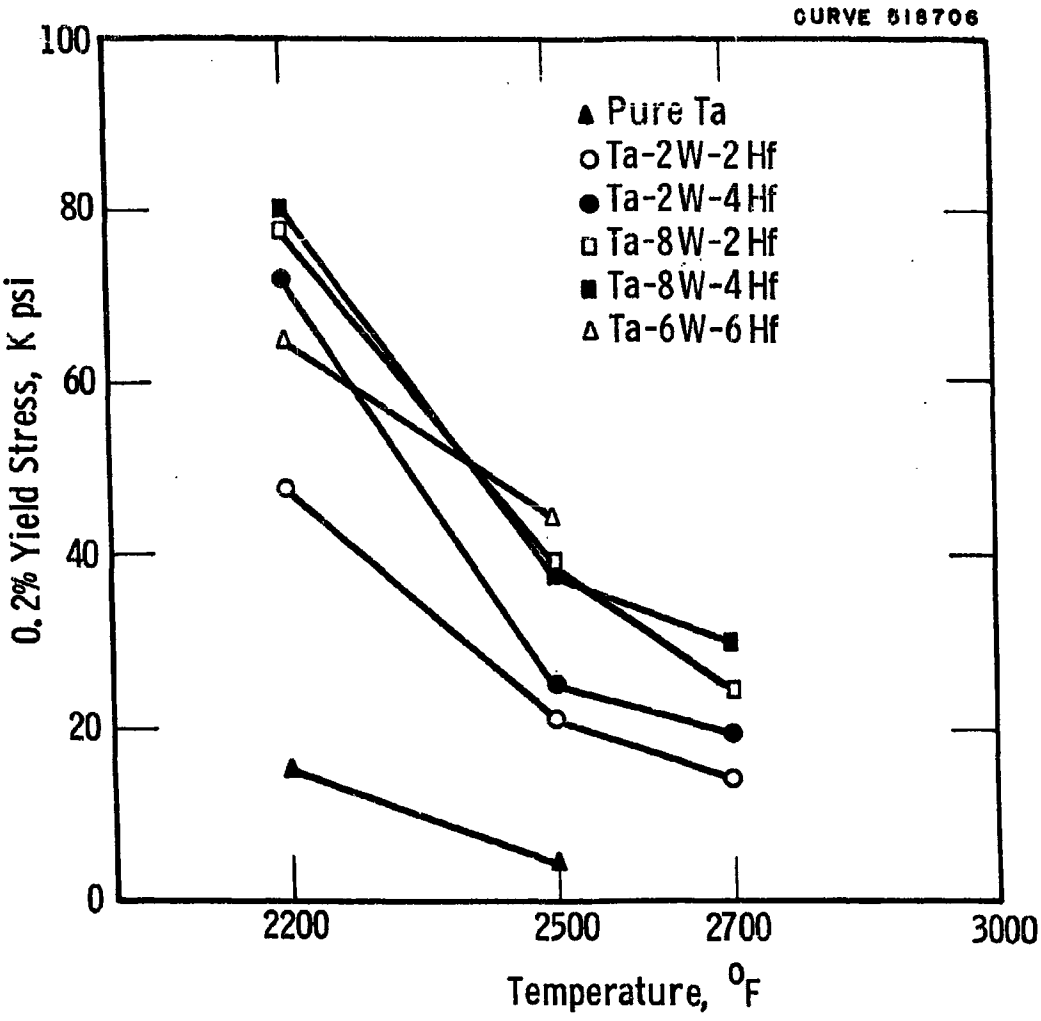

Fig. 64--Yield strength of Ta-W-Hf alloys as a function of temperature

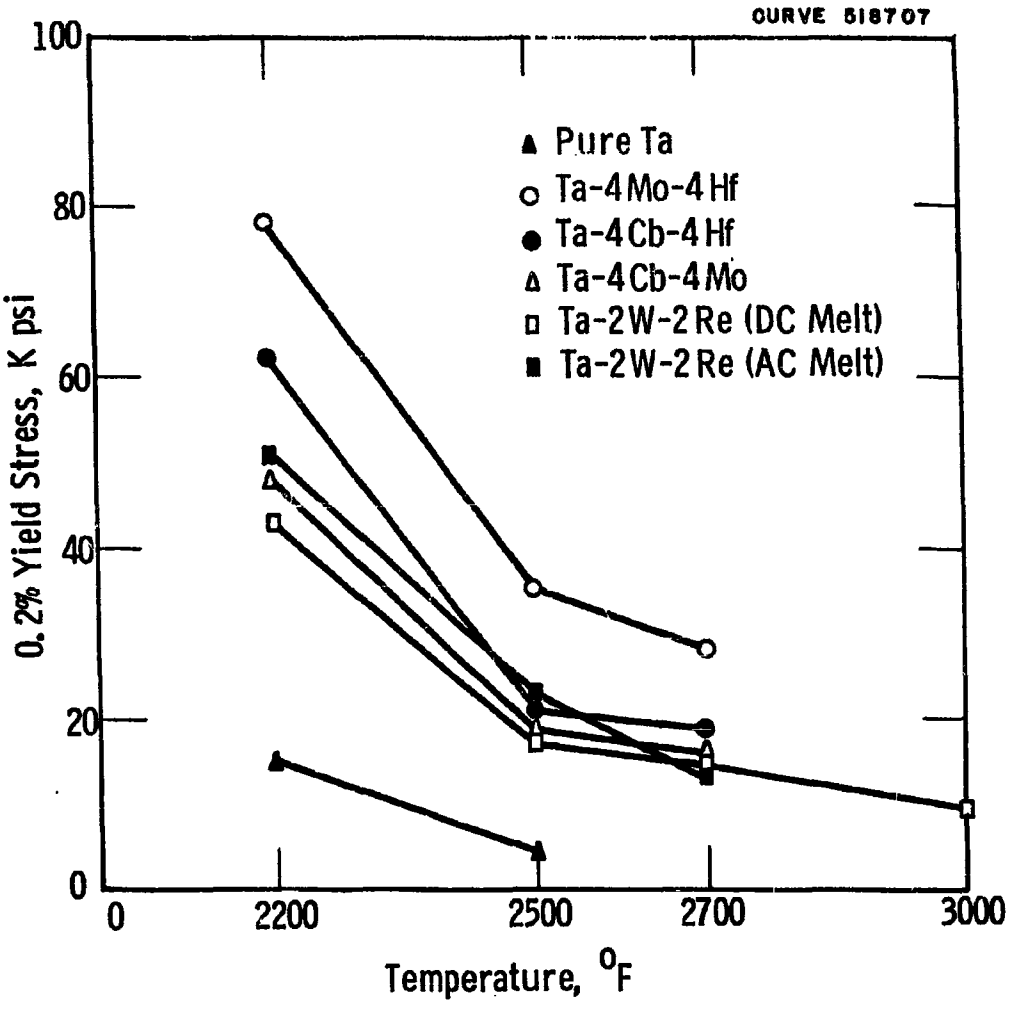

Fig. 65--Yield strength of Ta base alloys as a function of temperature

between the Ta-2W-2Hf and the Ta-2W-2Re alloys indicates that larger additions of Re may provide tensile properties as good as the more highly alloyed Ta-8W-2Hf or Ta-8W-4Hf. The decided inferiority of the two alloys containing Cb is also quite striking. As well as can be determined, the substitution of Mo for W in Hf-containing alloys did not seriously affect the properties, indicating that Mo could be used with a distinct weight advantage over the W-containing alloys.

The properties of the high strength alloys are compared with available data for other tantalum base alloys and also for the other refractory metals in Table XVII. The data in this table have been assembled from a variety of sources on materials in a variety of conditions. The data clearly show, however, that Ta-base alloys have a very competitive position at temperatures as low as 2200°F. At higher temperatures only the W-base alloys have properties superior to the Ta-base alloys.

B. TUNGSTEN BASE ALLOYS -- The work on W-base alloys carried out in this investigation has been much less extensive than that carried out on Ta. No mechanical properties other than hardness were determined. The oxidation resistance was cursorily determined for alloys containing Ta, Re and Hf. As expected, slight improvement was found for alloys containing Ta and/or Hf. The oxidation resistance of alloys containing Re was worse than that of W. The fabrication of a W-5Re alloy was also studied.

The addition of Hf to W increased the room temperature hardness in a normal fashion. The addition of Ta and Re to W had rather unusual effects, which will be discussed later. The addition of Ti, Zr, and V to W also increased the hardness. Because of difficulties in retaining these elements during melting, the resulting alloys were not homogeneous and no further work was done on these systems.

The addition of 2, 4, 8, or 16% Ta to W produced alloys of about 400 VHN hardness. Further increases in the Ta level then increased the hardness to a value greater than 500 VHN, followed by a smooth decrease in hardness to the hardness of pure Ta. The cause of the plateau in hardness

TABLE XVII. Mechanical Properties of Refractory Metals and Alloys

(Representative values only)

Alloy Designation and/or Developer	Composition (interstitials omitted)	Condition	Source	2200°F s/w ratio 10^3 inches	75°F UTS kpsi	75°F YS kpsi	75°F E %	2200°F UTS kpsi	2200°F YS kpsi	2200°F E %	2600°F UTS kpsi	2600°F YS kpsi	2600°F E %	3000°F UTS kpsi	3000°F YS kpsi	3000°F E %
-W	Ta-8W-4Hf	SR	1	152	147	140	15	91	80	23	37.6	34	58	----	----	--
-W	Ta-8W-2Hf	SR	1	142	135	130	15	85	78	15	41.5	31.3	45	----	----	--
-W	Ta-6W-6Hf	SR	2	130	----	---	--	78	65	15	41	37	15	----	----	--
-W	Ta-4Mo-4Hf	SR	1	147	144	139	16	85	78	26	34.1	31.7	69	----	----	--
-BMI	Ta-10Hf-5W	RX	3	108	115	105	23	64	--	6	37	25	17	17.8	12.1	29
-BMI	Ta-30Cb-7.5V	RX	3	142	139	125	27	61	48	35	36.1	22.3	76	10.2	6.2	99
-BMI	Ta-10V	RX	3	157	161	144	16	80	47	6	34.1	25.6	68	11.4	7.5	160
Numerous	Ta-10W	W	4	110	180	164	4	67	55	4	21	14.4	17	12.1	11.8	33
Numerous	Ta-10W	RX	4	67	90	84	29	41	--	13	----	----	--	----	----	--
F48-GE	Cb-15W-5Mo-1Zr	W	5	118	125	---	25	40	--	41	----	----	--	----	----	--
Cb-74-UCC	Cb-10W-5Zr	W	5	140	---	---	--	45	42	23	----	----	--	----	----	--
D31-DuPont	Cb-10Mo-10Ti	W	5	93	106	94	26	27	26	22	11	----	--	----	----	--
B77-W	Cb-5V-10W-1Zr	SR	6	141	127	107	15	45	38.5	49	19	17.5	90	----	----	--
-Climax	Mo-.5Ti	SR	7	103	115	98	12	38	29	50	17.6	11.4	11	10.3	6.2	25
TZM-Climax	Mo-.5Ti-.08Zr	SR	7	170	126	105	9	63	--	24	43	----	--	14	----	50
-W	W-2 ThO2	W	8	71	---	---	--	50	47	--	45	42	56	----	----	--
Numerous	W-30Re	RX	9	208	200	---	5	150	--	8	125	----	--	50	----	13
Pure Metal	Ta	RX	3	16	30.6	23.1	41	9.4	--	46	4.6	----	66	3.6	----	82
Pure Metal	Cb	RX	5	17	40	30	35	5	--	50	4	3	100	----	----	--
Pure Metal	Mo	SR	6	110	95	89	34	38	--	40	12	----	--	6	----	5
Pure Metal	W	W	10	---	---	---	--	--	--	--	42	----	--	21	----	48

1. This investigation - 2600°F interpolated
2. This investigation - 2600°F extrapolated
3. Schmidt et al - WADD-TR61-106
4. Schmidt-DMIC Report 133
5. Bartlett and Hauck-DMIC Report 125; Perlmutter and Lement-J. Less Common Metals
6. Begley et al - WADC-TR57-344, part V.
7. Hauck-DMIC Report 140
8. Atkinson et al - Detroit Symposium
9. Sims and Jaffee - Tr. ASM, 52
10. Sikora and Hall - NASA TND-79

UTS = Ultimate Tensile Strength
YS = 0.2% Yield Strength
E = % Elongation
s/w = Strength to Weight
SR = Stress Relieved
RX = Recrystallized
W = Wrought

is not known. The same phenomenon was found in W-Ta-Hf alloys within the solid solution range (4% Hf or less). This behavior is possibly due to a Ta-interstitial reaction, although no other evidence for this type of behavior was found.

The addition of Re to W produced a striking decrease in hardness. A similar decrease had been observed upon the addition of Re to Mo, and recently evidence of a decrease in hardness due to the addition of some of the group VIII elements (such as Os and Ru) to Mo had been reported. The alloy of minimum hardness occurs at about 5% Re.

The effect of Ta and Re additions on the elevated and subzero hardness of W was also very interesting. Fig. 66 illustrates the extreme effect upon hot hardness of quite small additions of Re and Ta. At the same time a decrease in the low temperature hardness was found. If the assumptions are made that a decrease in hardness is associated with a decrease in flow stress and that the temperature of ductile-to-brittle transition is related to the relative magnitudes of the flow stress and the brittle fracture stress, then a decrease in the ductile-to-brittle transition temperature should be found in these alloys. Based on previous observations, good room temperature ductility will certainly not be observed, but a slight improvement should be found. At the same time, a sizeable improvement in the high temperature strength should be found. The information presently available is insufficient to allow anything more than speculation as to the causes of these two effects.

C. CONCLUSIONS AND RECOMMENDATIONS

1. High strength Ta alloys can be easily fabricated using presently developed techniques.

2. Ta-base alloys, even in their present partially developed state, are competitive on a strength to weight basis at temperature as low as 2200°F with alloys of W, Mo, and Cb.

3. Further investigations of the fabrication and properties of Ta-base alloys based upon the systems discussed in this report should be

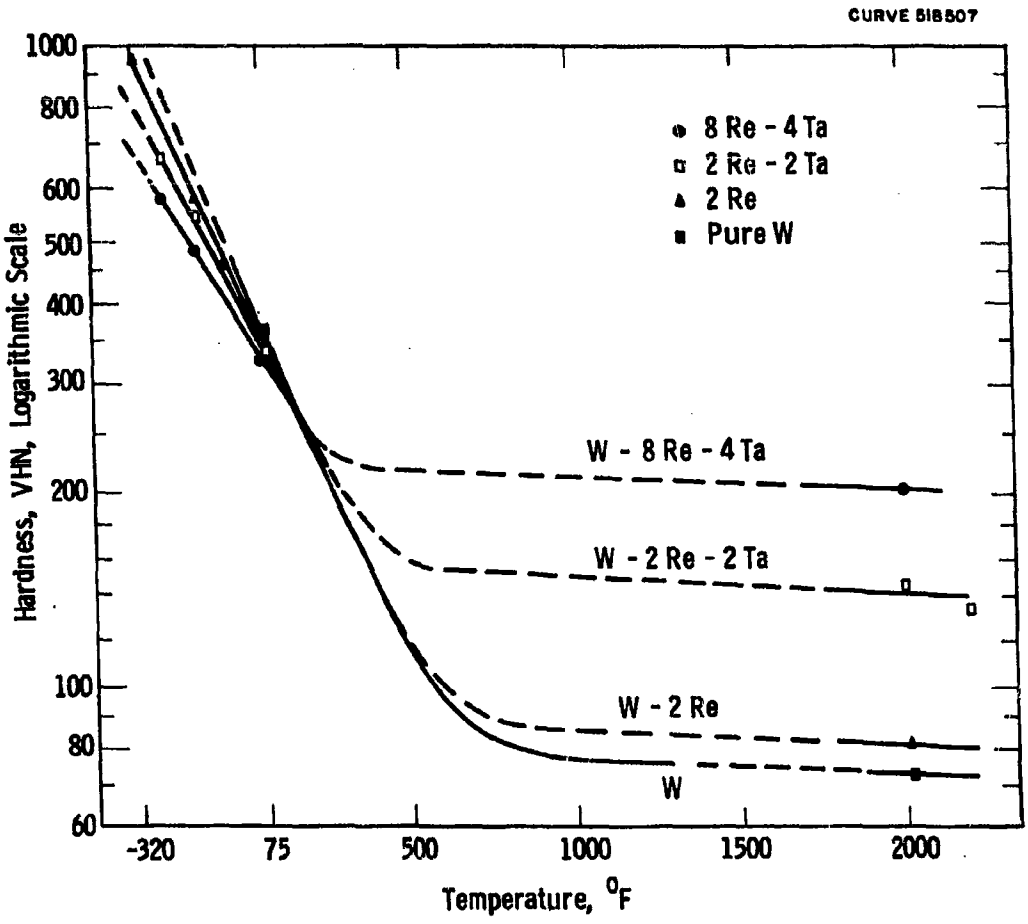

Fig. 66--Hardness of Tungsten-Tantalum-Rhenium alloys as a function of temperature

carried out. In particular, information should be obtained on workability, recrystallization temperatures, effect of interstitial levels, and effects of varying processing techniques.

4. The cause of the good retention of strength at elevated temperatures of Ta alloys containing Hf in combination with W or Mo should be determined.

5. The addition of Re and Ta to W may produce an alloy with improved room temperature ductility and improved high temperature strength. Substantiation of this rather speculative conclusion should be sought.

6. Further investigation of the behavior of W alloyed with Ta and Re should be made in order to determine the causes of the anomalous hardness behavior of such W-base alloys.

V. ACKNOWLEDGEMENTS

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APPENDIX A

EXPERIMENTAL EQUIPMENT

by

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The work performed in this investigation involved the use of specialized equipment, some of which required original design concepts to permit obtaining the property data included in this report. Since similar equipment may be usefully employed by others engaged in future work on refractory metal projects, it is worthwhile to present somewhat detailed descriptions of various major items of equipment which were used during the processing and testing portions of this program. The following sections present descriptions of the theory and operation of the more important pieces of apparatus.

Levitation Melting. This is a melting technique whereby electrically conductive specimens are suspended and melted in an electromagnetic field. The forces responsible for floating and the eddy currents which cause melting are induced by a high frequency current flowing through a coil which surrounds the specimen.

The process offers many advantages which are not found in the more conventional melting methods. Specimens can be melted conveniently and rapidly. Contamination caused by crucible contact is eliminated. Electromagnetic stirring promotes homogeneity of the melt. Moreover, many shapes such as rods, bars, slabs, etc. can be cast. Relatively small quantities, up to 100 grams of most metals, have been successfully levitated in atmosphere[1] or in vacuum.[2]

The advantages of directly casting sheet bars are obvious. Such bars can be used with little or no processing to obtain material for oxidation, workability, work hardening, aging and recrystallization studies.

Equipment available at the Westinghouse Research Laboratories was used to determine if tantalum and tungsten, with their alloys, could be levitation-melted prior to evaluation. A drawing of the levitation melting unit is shown in Figure 1. Construction and operation are described in recent publications.[1][2]

Small Specimen Arc Melting. A tungsten electrode, water-cooled copper hearth arc melting furnace was used to produce consolidated alloys in the form of small ingots or "buttons" weighing from 20 g. to 250 g. The non-consumable electrode technique was employed with argon selected as the inert gas at either atmospheric or sub-atmospheric pressures. The essential features of this type of furnace have been described many times in the literature. The body of the

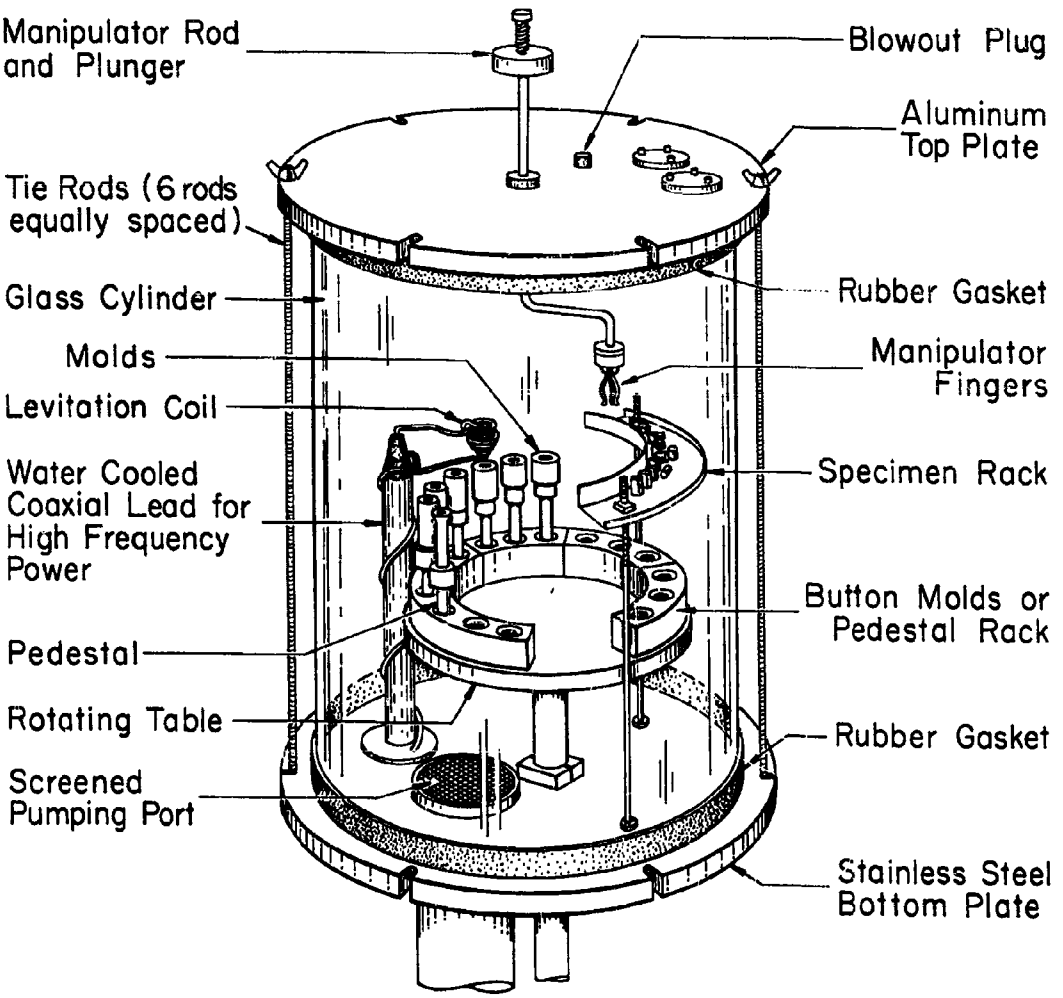

Fig. 1--Levitation melting furnace

furnace contains six removable hearths mounted on a revolving pedestal. Specimens of varying shapes, from round buttons to rectangular slabs, can be produced simply by using a hearth of the appropriate contour. Button melts are usually prepared, but longer rectangular slabs can be made for direct fabrication by rolling. A photograph of this equipment is shown in Fig. 2.

Consumable Electrode Furnace. A high vacuum arc melting furnace was used for consolidating tantalum and tungsten base alloys into cylindrical ingots about 2" in diameter and 4"-6" long. Like most furnaces of this type, it consists of four major components - the furnace itself, the vacuum system, the power supply and instrumentation and controls. The arrangement is shown in Fig. 3.

The furnace proper is composed of a tower-like structure housing a traveling carriage which supports the electrode holder. The carriage slides on a set of water cooled tracks from which it receives power for the electrode. The carriage is driven by an electric motor situated on the outside of the tower. A system of pulleys, shafts and gears transmits motion from the electric motor through a vacuum seal to the carriage within the evacuated tower. The electrode extends downward from the holder on the carriage into the main chamber, which is sufficiently water-cooled to prevent overheating of the furnace shell. This chamber serves as a juncture for several sight ports, the vacuum system opening and the receiver for the mold assembly. The mold assembly is of conventional design with water cooling provided for the mold wall and bottom. With the mold assembly in place, the top of the mold was originally in line with the centerline of the vacuum port for more efficient pumping during melting. However, this configuration had to be altered when excessive resistance heating of pressed tantalum base electrodes took place during melting. This heating of the electrode initially residing in the tower caused difficulty with auxiliary equipment located within the tower. Therefore, an extension piece was added between the mold assembly and melting chamber, thereby lowering the mold assembly. This modification permitted the whole electrode to reside within the water cooled main chamber and prevented overheating of the equipment within the tower.

The vacuum system is connected to the main chamber through a 10" diameter elbow which directs the gas stream downward through a spiral water cooled cold

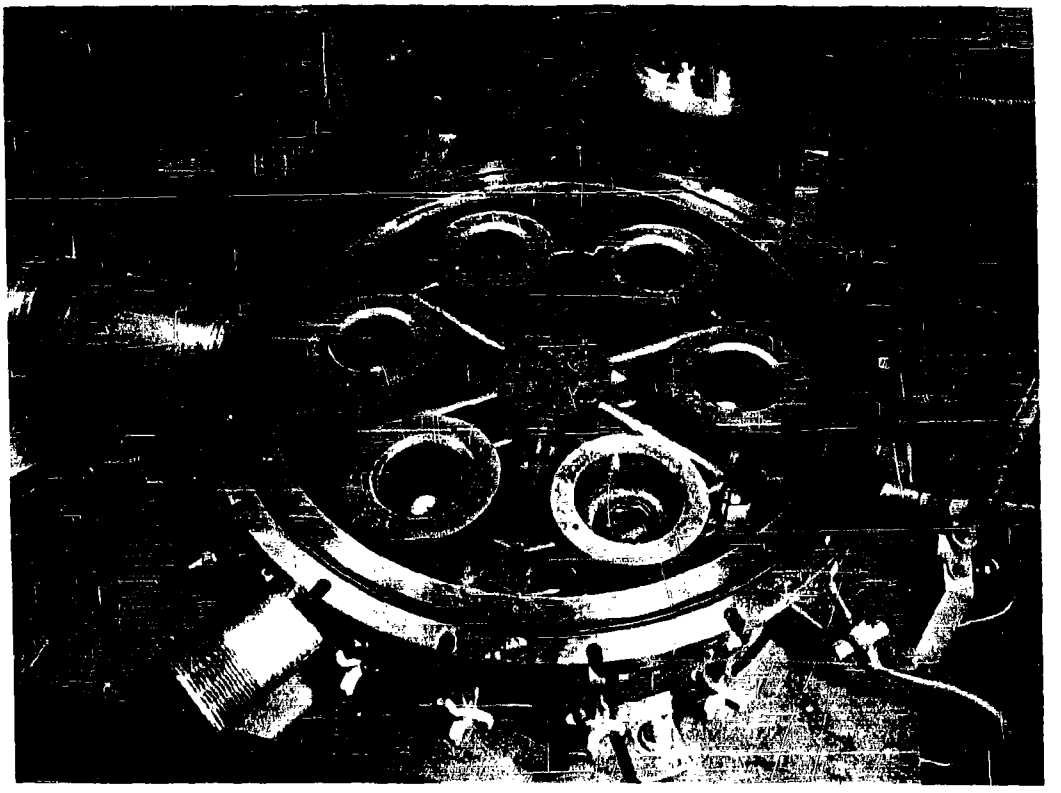

Fig. 2--Non-consumable arc melting furnace

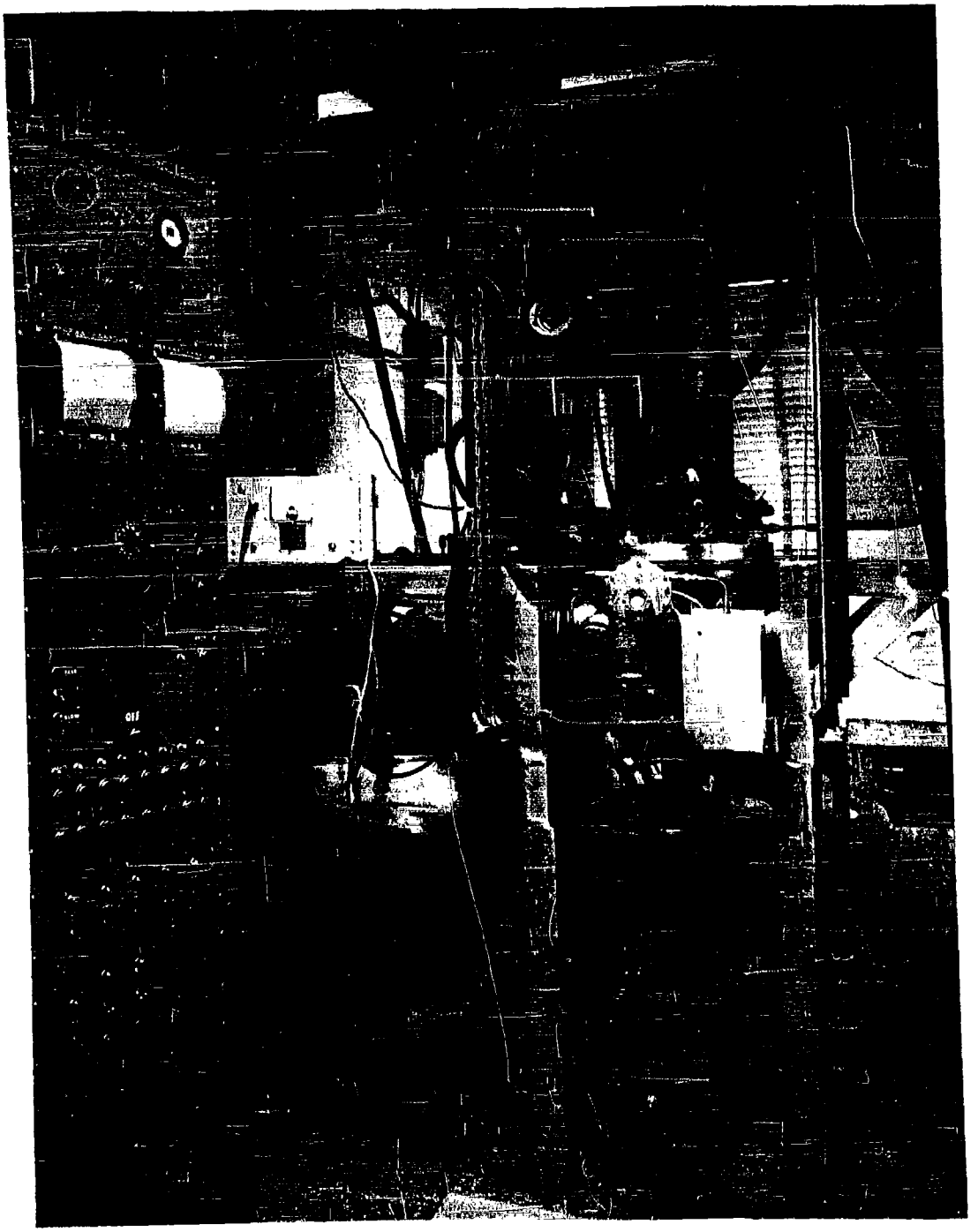

Fig. 3--Consumable arc melting furnace

trap. A 10" slide valve is located between the bottom of the elbow and the top of the Leybold Model OT1800 diffusion pump. A Kinney Model KD130 mechanical vacuum pump is used to back up the diffusion pump. This diffusion pump has a pumping capacity of 400 liters per second at a pressure of 10 microns. The mechanical pump has a capacity of 90 cubic feet per minute at 50 microns pressure. This vacuum system is capable of producing a furnace vacuum of .01 micron within an hour. The leak rate of the system was normally less than 1 micron-liter/second an hour.

The power supply is composed of both DC and AC welders. The DC apparatus consists of four double and four single Westinghouse Type RA selenium DC welders. The units operate from a 440 volt, 3 phase, 60 cycle AC source and deliver a maximum current at 40 volts of 400 amperes each, giving a total capacity of 4800 amperes. The large number of DC welders lends versatility to this type of melting. The welders can be preset at a given current level and can be cut in or out of the circuit during the melt to give the desired power input. The AC apparatus consists of two type RTA 60 cycle single phase welding transformers rated for 1000 amperes each at 40 volts load. This nominal 2000 ampere total can be boosted to almost 3000 amperes output with load voltages between 20 and 30 volts and with open circuit e.m.f. boosted to 100 volts from the normal 80 volts. The AC power supply was installed toward the end of the investigation when it became clear that melting of small tantalum and tungsten base alloy ingots in the research furnace was not possible using DC power.

The electrode feed rate is controlled by means of the voltage drop across the arc gap. Using a Westinghouse Weld-O-Matic controller, the arc gap voltage is compared with a preset reference voltage. A signal from the Weld-O-Matic causes the electrode drive motor to run in the appropriate direction to maintain the preset voltage.

Operation of the furnace is controlled from a vertical console which contains the indicating and recording equipment along with necessary power control switches. Melt chamber pressure, arc voltage, arc current and electrode feed rate are permanently recorded. Each individual AC or DC welder has an

"ON-OFF" switch and there is an emergency switch which shuts off all power at one time.

Induction Annealing Furnace. Phase I and Phase III button melts were annealed 16 hours at 2000°C in an induction heated vacuum furnace. A 10 Kilocycles per second motor-generator set supplied the high frequency current. Two CVC MCF 300 diffusion pumps backed up by a Welsh Duo Seal mechanical pump easily maintained a vacuum of 10^{-5} mm Hg at this temperature. Approximately 12 hours are required for this system to cool to room temperature. This furnace enabled a number of specimens to be annealed simultaneously.

Resistance Type Vacuum Annealing Furnace. Some of the high temperature annealing treatments of alloy specimens were carried out in a vacuum furnace capable of reaching temperatures of 3000°C. A detailed description of this furnace may be found in a previous technical paper.(3) The equipment consists of three separate parts - a vacuum system which includes pumps, valves, cold trap and furnace tank; the furnace itself, attached to the cover of the vacuum chamber; and the power source. A photograph of this equipment is shown in Fig. 4.

The vacuum system utilizes a Kinney KC-15 mechanical pump, a CVC-300 oil diffusion pump and a liquid nitrogen cold trap. A vacuum of .004 micron was obtained at room temperature and at 2000°C the pressure did not rise above .01 micron. The furnace tank is a 9-inch diameter water cooled copper pipe. The top of the tank contains a water-cooled brass plate in which are mounted an observation port, a specimen hanging device and electrode connections for the heater. Details of the furnace heater assembly are shown in Fig. 5. The heater assembly is made of tantalum, but the heater tube itself can be made of tantalum or tungsten, depending upon the temperature at which the furnace is to be operated. The heater used in this work was a split tungsten tube rolled from sheet about 10" long with a .030" wall thickness. Power was supplied by a 75-KVA transformer operating from 0-570 volts and controlled by a 32 KVA autotransformer. The heater tube itself is supported by a 1/4" thick tantalum plate bolted between the two long water cooled electrodes. The bottom electrode holds the heater tube. The shielding is of .005" thick dimpled tantalum sheet

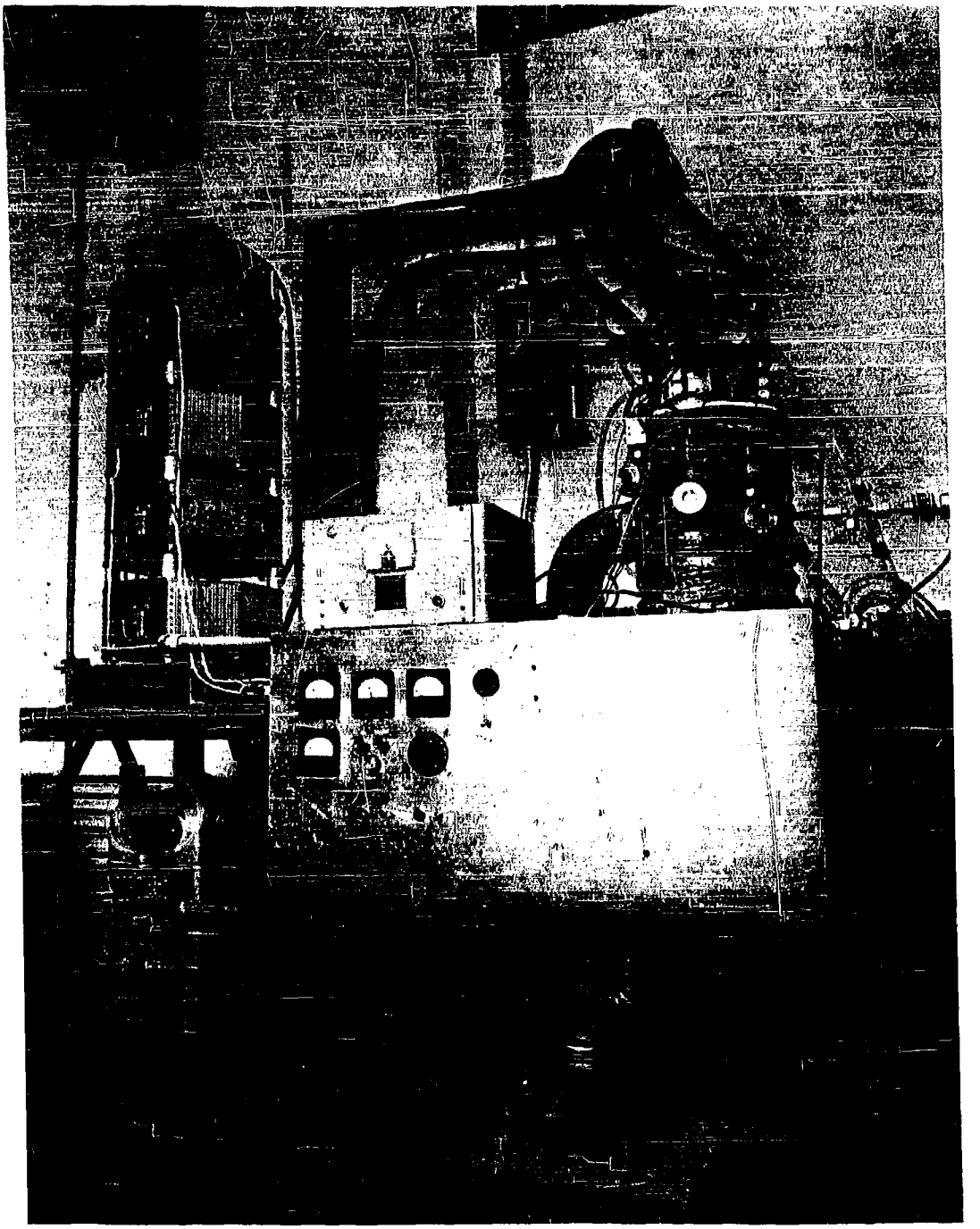

Fig. 4--Vacuum annealing furnace

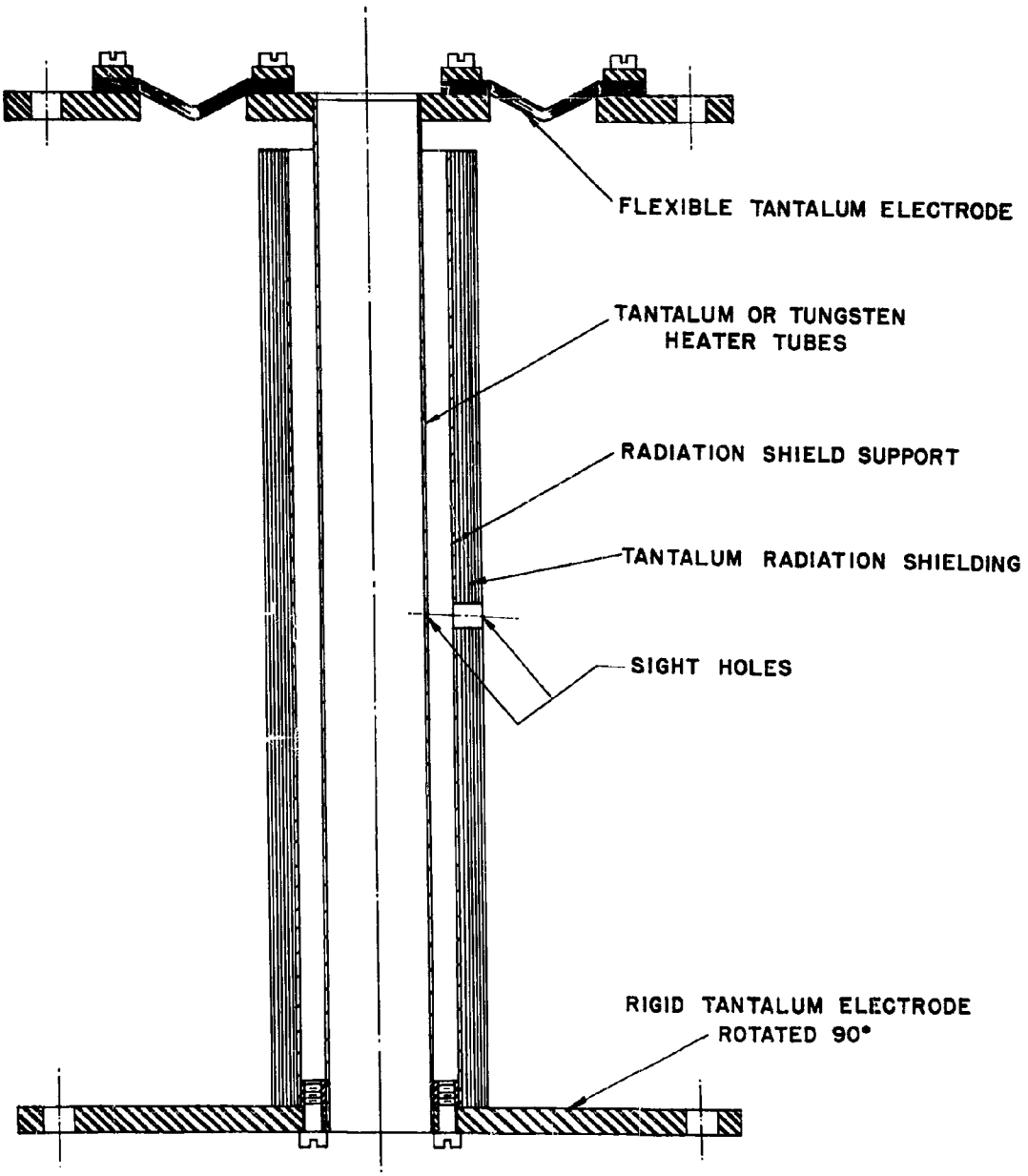

Fig. 5--Vacuum annealing furnace heater assembly

wrapped in a coil and supported on a cylindrical tube concentric to the inner heater tube. The flexible top electrode, made entirely of tantalum, permits the heater tube to expand at high temperature without damage to the tube. The heater is connected to the tantalum electrodes at both ends using only a friction fit. Tantalum radiation shields also are placed on the bottom of the furnace chamber and in the tube leading to the top sight port in order to minimize loss of heat through the ends of the heater tube.

Dynapak High Speed Extrusion Press. The Dynapak is a high energy-rate device which has appeared on the metal-working scene within the past several years. Because of its recent appearance and unique operation, the following description of the Dynapak is included here for the benefit of those who may be unfamiliar with the operation of this machine.

The model 1210 Dynapak (shown in Fig. 6) manufactured by the Convair Division, General Dynamics Corporation, is capable of producing high energy, 151,000 foot-pounds, within a short distance, 12 inches, and short times, 5 to 10 milliseconds. One attractive feature of this device is that it does not require a massive foundation, since all the energy not used in the metal working process is dissipated within the machine itself. Its relatively small size makes it ideal for laboratory or pilot plant installation.

The Dynapak derives its power from the controlled adiabatic expansion of a gas at high pressure. The heart of the Dynapak is the triggering device which allows a given volume of gas at high pressure to act on the driving piston almost instantaneously. A clear picture of the operation of the Dynapak can be obtained by following a complete operation cycle using the sectional drawing in Fig. 7.

The Dynapak is mounted on a recoil system in such a manner that the active part of the machine is allowed to operate as a free body. When the Dynapak is used as an extrusion press the ram piston, column, weight and punch assembly are forced to the top of their travel by gas at low pressure, usually 100 psi in the lower chamber. The working gas at pressures up to 2000 psi is introduced into the upper chamber and is separated from the piston by the firing

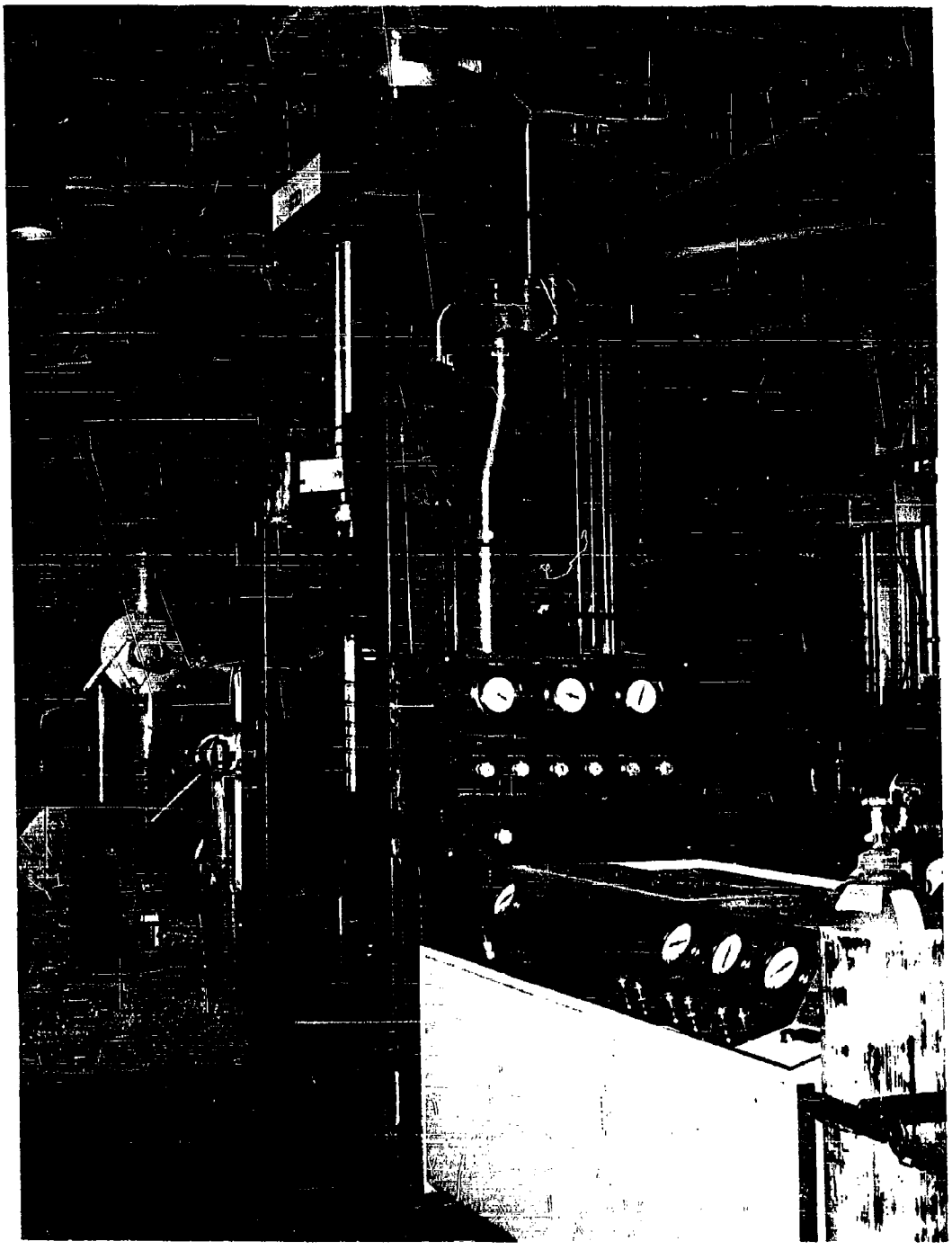

Fig. 6--Model 1210 Dynapak

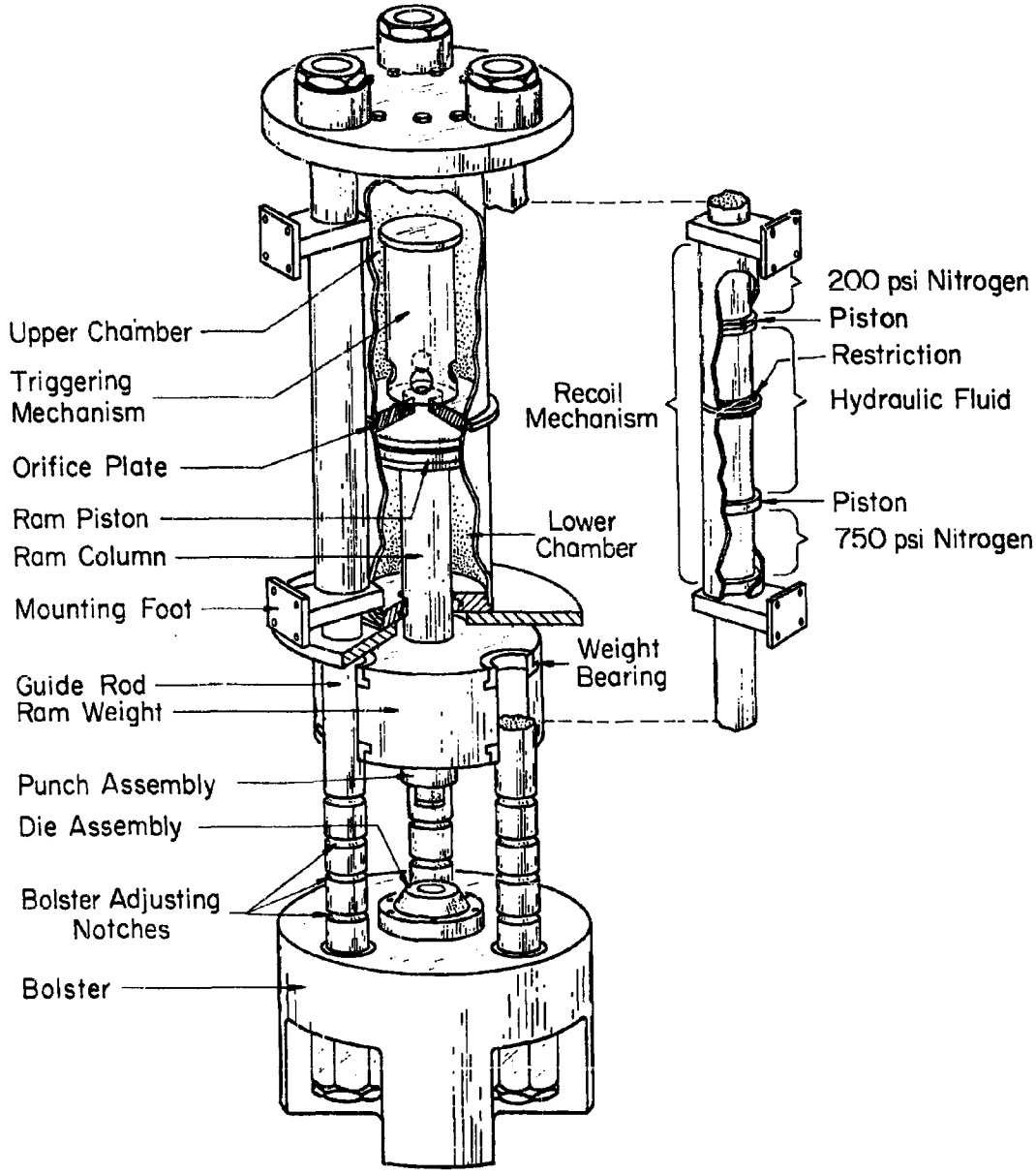

Fig. 7--Schematic drawing of Dynapak - Model 1210

mechanism and orifice plate. The amount of energy made available for the extrusion process is proportional to the gas pressure in the upper chamber and is a function of stroke length, as shown in Fig. 8. Activation of the firing mechanism allows the high pressure gas to pass through the orifice plate and act on the whole surface of the piston, creating a large unbalanced force which drives the piston, column, weight, and punch downward. Since the machine is essentially a free body, a reaction force equal to the force driving the piston acts on the top plate of the upper chamber and causes it to move upward along with the guide rods and bolster. This reaction mass is much larger than the mass of the weighted ram assembly and therefore moves at a proportionally lower velocity. As the piston moves downward the driving pressure begins to decrease adiabatically while the back-up pressure in the lower chamber increases, also adiabatically. The net pressure difference across the piston continues to drive the ram assembly downward while the reaction force continues to drive the reaction mass upward. After traveling several inches the punch asembly attains a high velocity relative to the die assembly on the bolster. In the extrusion operation a billet in the die assembly receives the full impact of the ram and if all conditions are favorable the billet extrudes through the die, consuming the kinetic energy of the system. Hydraulic fluid is then pumped into the lower chamber beneath the piston to return it to its original position.

From the description of the apparatus given above, it is apparent that the firing pressure must be selected carefully before the extrusion process is initiated. There is no opportunity to adjust pressure once the Dynapak has been fired. If, for a given set of conditions, the initial pressure is too low the billet will not be completely extruded. If the initial fire pressure is too high the billet will extrude completely, leaving the die at high velocity with the excess energy of the machine absorbed by the damping effect of the guide rods. With a high exit velocity it is difficult to decelerate the extrusion without damage.

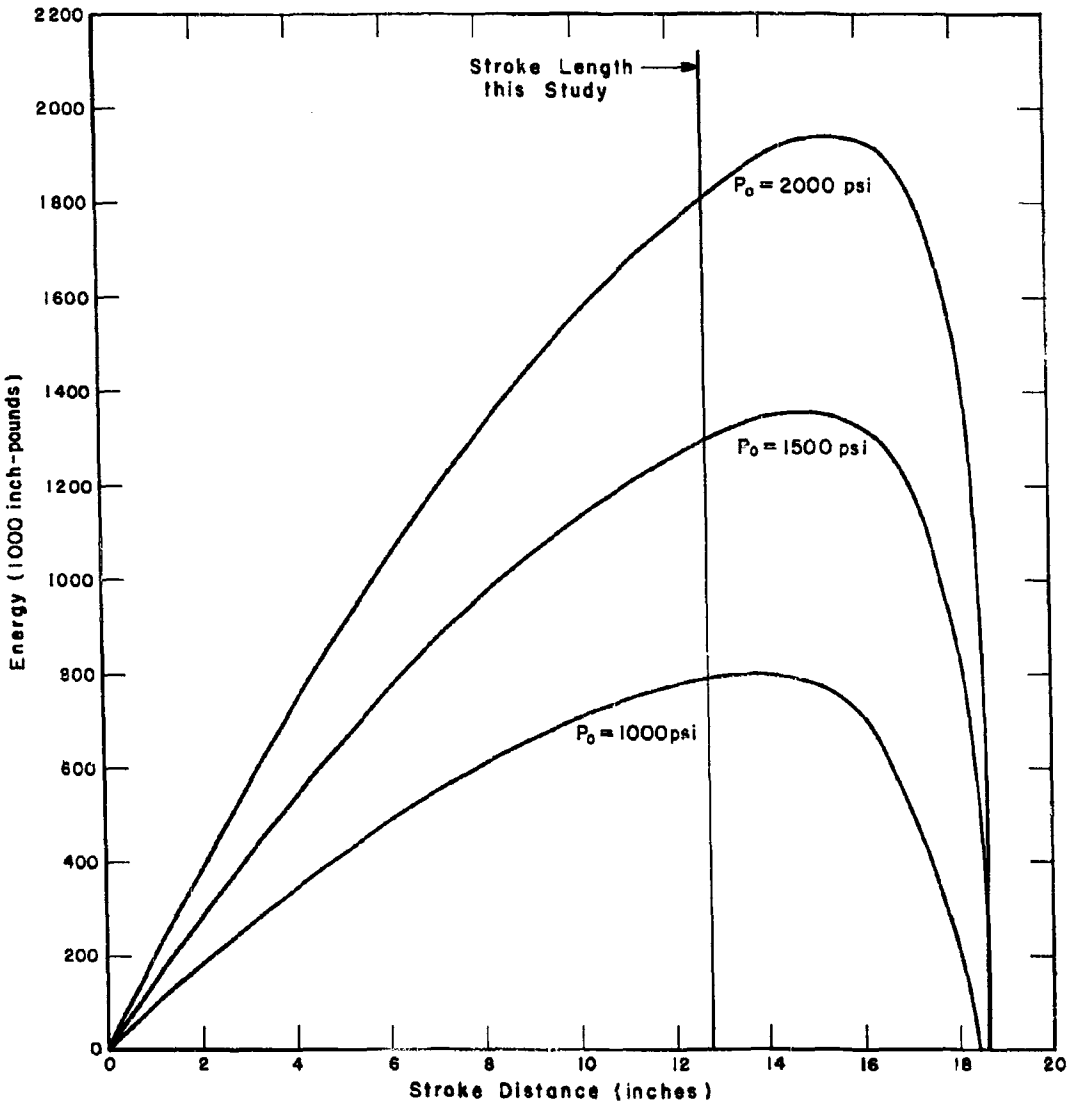

Fig. 8--Available energy as a function of stroke length

To maximize the yield of sound material, it is necessary to completely extrude the entire billet through the die in such a manner that the resulting extrusion can be safely decelerated without damage. The amount of excess energy absorbed by the guide rods must also be kept to a minimum to prevent damage to the machine. Selection of the energy level which will achieve the desired results is greatly influenced by many operating variables. For extruding a given material, these variables include ram and reaction masses, total stroke length, extrusion ratio, die geometry, lubrication, extrusion temperature, billet length (volume), back-up pressure and initial fire pressure.

For the particular Dynapak (model 1210) used in this work, the ram and reaction masses were fixed by the construction of the machine. Stroke length was limited to 12.5 inches. Die geometry, extrusion ratio, and lubricating procedure developed for the extrusion of columbium-base alloys to sheet bars were utilized.[4] The die, represented in Fig. 9, was made from an AISI-H-13 tool steel and heat treated to a hardness range of R_c 46 to 49. The die cavity was 1/2 inch by 1-1/2 inches wide, producing a 4:1 extrusion ratio.

To provide lubrication for the extrusion process, a slurry consisting of a mixture of fine glass powder (Corning 7052) and alcohol was painted on the billet container, die face and on the billet before heating to extrusion temperature. To provide additional protection for the die, a plain glass wool pad was placed on the die face. The die, die holder, and billet container were not heated for the extrusion operation.

It was decided that all alloys would be extruded at 1700°C. At this temperature, it was believed that the alloys would require a comparable flow stress, neglecting strain rate effects. Past experience indicated that energy at the rate of 20,000 foot-pounds per cubic inch of extrusion billet would provide enough energy to extrude the alloys completely without damaging the equipment. With this criterion for the given conditions, required energy levels for billets of differing lengths were easily determined. Back-up pressure in the lower chamber was maintained at 100 psi for all extrusions.

This method of high energy rate extrusion was found to be very satisfactory for the primary breakdown step in the production of round or rectangular bar stock from cast ingot stock.

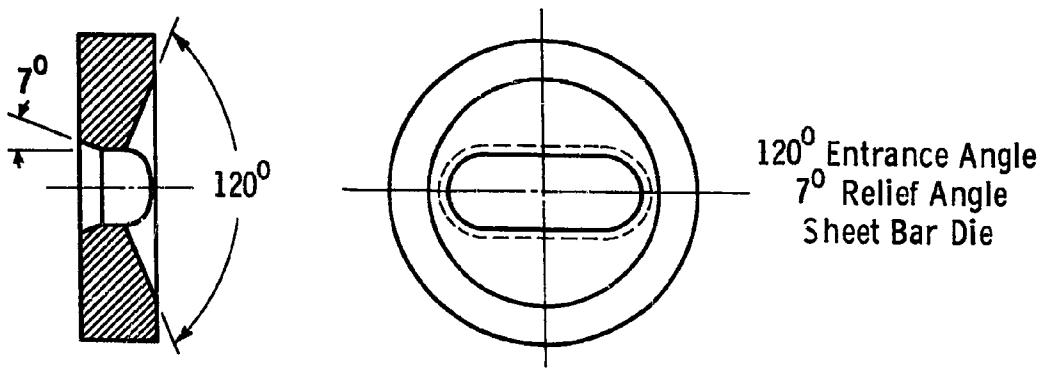

Fig. 9--Configuration of Dynapak extrusion die

Forging Hammer. The forging equipment used to evaluate the hot workability of tantalum and tungsten alloy buttons was an 800 lb. steam operated hammer forge. Flat open dies were used. The specimens were placed on the lower die and the upper die was allowed to fall freely under the influence of gravity to impart one measurable blow to the specimen. Therefore, this equipment was used more as a drop test rig than as a true forging machine.

Rolling Mill. The rolling mill used to process extruded rectangular bars was an 8" x 8" two-high laboratory reversing mill. A variable speed of from 10-200 surface feet per minute is available. The mill drive is of 25-HP capacity. Forged Ni-Cr-Mo steel flat rolls were employed for the experimental rolling program. A resistance heated electric furnace in close proximity to the mill was used to heat material to the rolling temperature.

Hot Hardness Tester. Engineering data are usually obtained using short time tensile and creep-rupture testing procedures. These types of tests are expensive, time consuming and require considerable amounts of material for evaluation. Therefore, they are undesirable for screening large numbers of alloys, especially for elevated temperature applications where numerous tests are required. A simpler criterion, that of hardness, is being used successfully as an indication of strength of materials over wide temperature ranges. Hardness testers have been used by a number of investigators and data have been obtained from -150°C to 1600°C for many materials.

To facilitate screening of high temperature materials, particularly the alloys investigated under this contract, a hot hardness testing machine capable of operation at temperatures up to 1200°C was designed and constructed. The equipment will be described in some detail since it has not been reported in the literature, and it did play a major role in the alloy screening phases of the contract.

The essential features of the instrument are shown in Fig. 10. The main vacuum chamber is a water-cooled stainless steel tank approximately 12" in diameter and 17" long. The upper and lower flanges, also water-cooled, are bolted and sealed by "O"-ring gaskets. A 4-in. diameter vacuum line is connected to the mid-height of the tank and exhausts the system through a CEC MCF-300

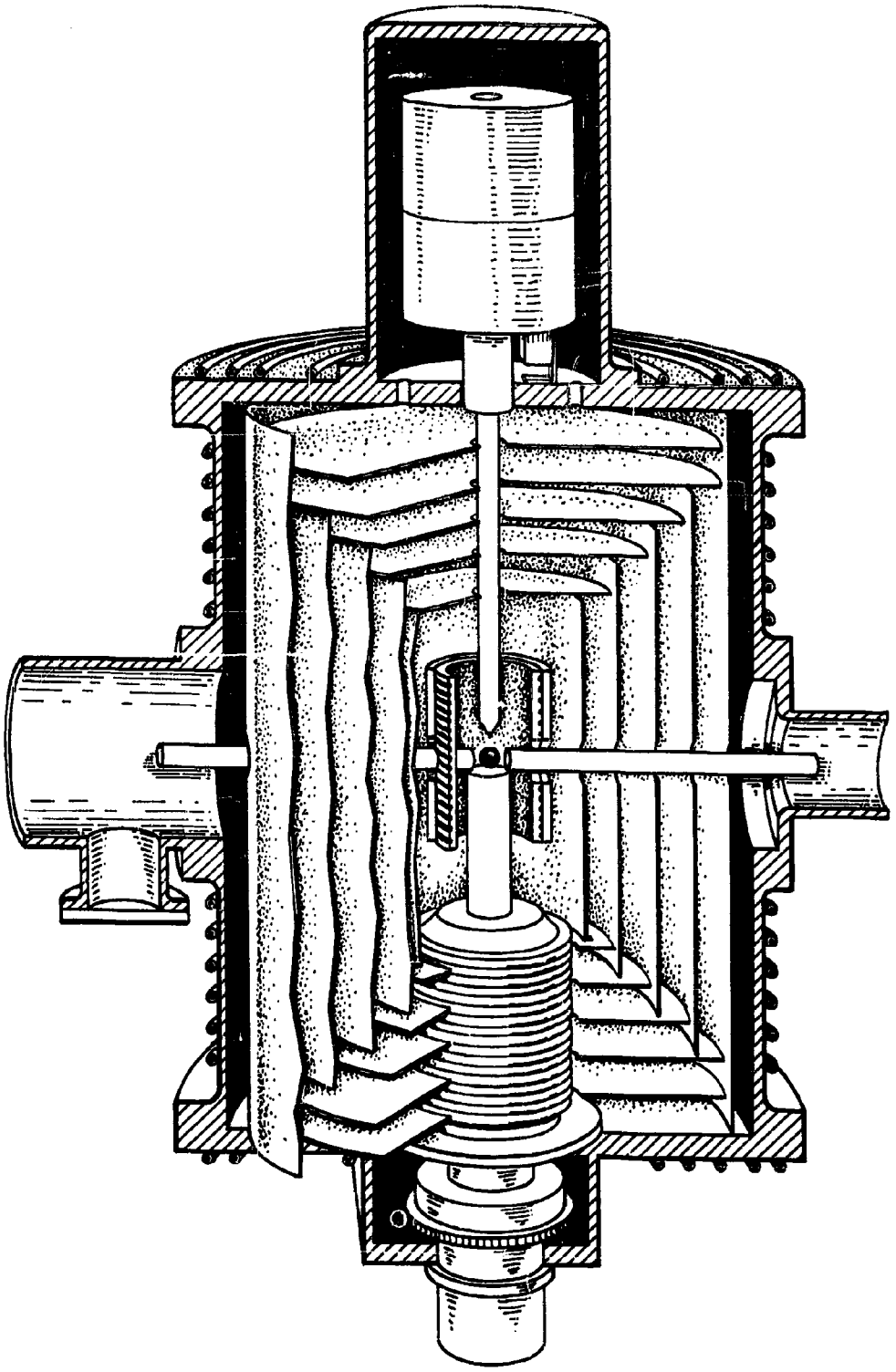

Fig. 10--Hot hardness tester

diffusion pump and a Kinney KS-13 mechanical pump. A 4-in. slide valve isolates the pumping system from the main chamber. A liquid nitrogen cold trap between the diffusion pump inlet and the chamber entrance minimizes oil backstreaming and permits a higher vacuum to be obtained. In practice, the apparatus can be evacuated to a pressure of .02 micron at room temperature and to less than 0.1 micron at 1200°C.

The specimen heating furnace consists of an alumina sleeve wound with molybdenum wire which is electrically resistance-heated. Maximum temperature capability in the 2" diameter by 4" long hot zone is approximately 1600°C. The heating chamber is surrounded by five sets of molybdenum radiation shields. These shields are designed to protect top and bottom openings of the heating chamber from radiation losses as well as the sidewalls of the chamber.

The specimen support assembly is bolted to the bottom flange and extends up through the lower radiation shields, terminating in a specimen stage located in the center of the heating chamber. The support assembly incorporates a bellows arrangement which allows the stage to be raised and lowered slowly by a motor driven shaft which extends to the outside of the machine through a vacuum tight connection. The indenter assembly extends downward through the top radiation shields. It consists of a sapphire indenter bonded to a molybdenum shaft which in turn is connected to a 12" long stainless steel tube. The stainless tube is held in rigid alignment by a long ball-bearing bushing mounted on the top flange of the main tank. On top of the indenter, in an auxiliary chamber, are mounted the proper weights to give the desired total load on the indenter. The sapphire tip of the indenter, ground in the shape of a 136° pyramid, is normally separated from the top of the specimen stage by one inch of space. The specimen itself is 1/2-inch in height. Therefore, the stage only has to be raised slightly more than 1/2 inch to cause the specimen to contact the indenter and lift the weight off the "rest" position.

A total of 10 specimens may be placed in the machine at one time by means of an unusual loading assembly. An entrance chamber is located on the opposite side of the main tank from the vacuum line. The samples are loaded into a rectangular channel and can be pushed one by one to a small transfer table. A

vacuum sealed push rod located at a 90° angle to this feed channel is used to push an individual specimen down another channel to the specimen support stage. Alignment of the specimen under the indenter is made visually, utilizing a sight port in the chamber wall for that purpose. A micrometer adjustment permits accurate specimen positioning. Several impressions can be made before the specimen is pushed into a continuation of the original feed channel which terminates in a small flanged trap located in the inlet to the main vacuum line. After all pieces have been tested, the trap may be opened to remove them.

In operation, the specimens are loaded and the equipment is pumped down cold to the low micron range. The first specimen is maneuvered to the stage and the furnace is turned on. Temperature control is obtained by means of a platinum thermocouple and proportioning-type controller. Temperature is recorded on an L & N Speedomax unit. When equilibrium temperature is reached, the motor drive of the indenter assembly is actuated and the support stage is raised until the indenter load is impressed on the specimen. The load can be 1, 2.5 or 5 kilograms depending on the specimen material and test temperature. The dwell time for the load is 15 seconds, after which the stage is lowered and the weight removed. Hardness impressions are measured at room temperature. No correction is made for impression shrinkage due to thermal expansion, but the error involved is less than the limits of accuracy imposed by other variables in the system.

Since the specimens used were primarily halves of arc-melted buttons, the problem of providing a stable support for the specimen arose. Attempts to solve by mechanical mounting proved unsatisfactory. The final solution was to support the irregularly shaped specimen with Ta powder within a 1/2 to 5/8 inch die, and press the entire assembly at 170,000 psi. This procedure is quite similar to the normal metallographic mounting procedure, except that Ta powder is substituted for organic mounting material (e.g. Bakelite). The mounts had very good green strength.

The mounted specimens were then ground to provide parallel sides on top and bottom. Since a brief investigation had indicated that the surface condition would affect the hot hardness readings, all specimens were

metallographically polished and etched. After rinsing in acetone, the specimen and mount were annealed at 900°C for 1 hour. This annealing treatment removed any residual entrapped moisture from the polishing and etching, relieved any residual stresses in the sample resulting from the high pressure mounting, and imparted a certain amount of additional strength to the Ta powder mount.

Cold Hardness Tester. The cold hardness tester has been described in a recent publication.[5] The apparatus can be used to make Vickers hardness impressions from room temperature to -320°F.

This equipment was built to overcome the problem of continuously varying the test temperature in a low temperature bath. A standard Vickers hardness machine was modified by replacing the conventional indentor with an extended indentor and by removing the calibration plug to compensate for added indentor weight. Nitrogen vapor enters the test chamber through a perforated copper coil wound around the anvil, specimen and bottom of the indentor. The Dewar flask is designed so the pressure build-up above the liquid nitrogen in the flask forces the liquid through the supply line to the perforated cooling coil.

The flow and temperature control system consists of a needle valve, a packless magnetic valve, an anticipating type temperature controller and recorder, and a copper-constantan control thermocouple. The thermocouple bead is placed in a small hole on the surface of the specimen to avoid any direct contact of the bead with liquid nitrogen. The magnetic valve is opened upon demand for heat removal, and nitrogen vapor is supplied to the anvil, sample and indentor. The flow is regulated by the needle valve. The specimen temperature can be controlled to $\pm$ 4°F over the range from room temperature to -320°F.

The test chamber anvil is parallel to the base of the test chamber, and specimens are prepared so as to have opposite faces parallel. Thus, it is not necessary to level each specimen prior to making impressions. The chamber is mounted on a traversing stage which permits a series of impressions to be made easily. Hardness determinations, using a normal Vickers cycle, can be made for several test temperatures on the same specimen by simply moving or rotating the chamber.

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APPENDIX B

METALLOGRAPHIC PROCEDURES FOR TANTALUM, TUNGSTEN AND THEIR ALLOYS

by

Roy L. Anderson

This work on the metallography of tantalum and tungsten has been a part of a much larger program involving certain metals which are referred to as refractory metals. The term refractory metals includes the platinum metals and the metals of groups IV, V, VI, and VII of the periodic table which have melting points above 1500°C.

Part of the work in this general area has involved a reappraisal of methods which have been in use for many years. Both tantalum and tungsten have been known for over a hundred and fifty years. Until quite recently, tantalum was rarely used and tungsten was used principally as a filament material and as an alloying element in steelmaking.

Published methods for the metallographic preparation of both metals also date back at least 30 years. Apparently, due to the problems attendant to its use in filaments, tungsten has received a much more careful metallographic study than has tantalum. Despite these facts there still remains a great deal of work to be done on the metallography of both metals and their alloys. This report describes practices currently employed at the Westinghouse Research Laboratories.

Before attempting to develop metallographic procedures for any metal its chemical and physical properties should be carefully reviewed, particularly in the areas which would be of interest to a metallographer. Such studies usually reveal sensible lines of approach and the areas in which experimentation would probably be fruitless. Since there is very little chemical similarity between tantalum and tungsten, they will be taken up separately.

Tantalum. Tantalum with its sister elements, vanadium and niobium, falls in group V-A of the periodic system. Owing to the lanthanide contraction, tantalum and niobium have nearly the same atomic volume and the two metals are very similar to each other in chemical and physical properties. Neither metal resembles vanadium as much as they do each other.

Pure tantalum is soft and ductile but by suitable cold working procedures its hardness can be increased greatly. It can be embrittled by a small amount of hydrogen. Under proper conditions it is also a good scavenger for oxygen and nitrogen.

Tantalum pentoxide (Ta_2O_5) is the only oxide of importance although lower oxides are also known. The pentoxide is formed by heating tantalum in air, or by heating the hydrated oxide. It is colorless, inert and extremely stable. When tantalum is electrolyzed in any electrolyte except a fluoride, an oxide film is formed which is a very effective rectifying barrier.

Although tantalum is amphoteric no hydrates of it are known. Most of the tantalates come from the metal and $HTaO_3$. The tantalates are generally insoluble, even those of the alkali metals. However, the alkali salts of $H_8Ta_6O_{19}$ are somewhat soluble.

Tantalum forms pentahalides with the halogens, all of which are hydrolized by water. It also forms many fluotantalates. It forms no salts with the oxygen acids. The metal is dissolved only by hydrofluoric acid, fuming sulfuric acid and fused alkalis. The halides are generally soluble in absolute alcohol without decomposition.

Tungsten. Tungsten falls in group VI-A of the periodic table in the family with chromium and molybdenum. Again due to the lanthanide contraction, the atomic volumes of tungsten and molybdenum are very similar and these metals resemble each other more closely than they do the other member of the family.

Tungsten is very resistant to most acids including hydrofluoric but it is slowly attacked by a mixture of hydrofluoric and nitric acids. It has a very slight solubility in nitric acid, sulfuric acid, and aqua regia. It is also very slowly soluble in a solution of potassium hydroxide.

Tunsten forms two definite oxides, WO_2 and WO_3. Tungstic acid, H_2WO_4 corresponds to the trioxide and is probably the basis for most of the etching reactions used with tungsten. Most of the tungstates are insoluble. Ammonium tungstate is unstable and easily gives up NH_3. Paratungstates, $5M_2O \cdot 12WO_3 \cdot nH_2O$, and metatungstates, $3M_2O \cdot 12WO_3 \cdot nH_2O$, are also definite compounds of which the alkali metal and magnesium compounds are soluble.

It forms halides with bromine, chlorine and fluorine, all of which are hydrolized by water. For this reason these reactions are not of much use in metallographic etching.

Metallographic Procedures - General. The metallographic preparations of tantalum and tungsten are two entirely different problems. The metals resemble each other only in their melting point and their ease of oxidation at elevated temperatures. Because both metals are difficult to grind, polishing them requires a great deal of time. Certain general procedures will be considered first after which specific procedures will be given for each metal.

There are many advantages to be gained by mounting specimens for metallography. The use of mechanical aids to preparation also requires that virtually all specimens be mounted.

The refractory metals project has required the specimen to be prepared, photographed and recovered for further heat treatment, followed by subsequent re-examination. This places the stipulation on any mounting material that the specimen can be removed in one piece; thus thermoplastic materials such as lucite must be used. Mounting in lucite is a time-consuming operation. A material which is suitable for the purpose is called "Kold Mount." * Kold Mount consists of a powder and a liquid, presumably lucite powder and the monomer of methyl methacrylate. These are mixed and poured over the specimen in a suitable mold. The mounts are ready for use in about twenty minutes. Suitable molds are made by cutting 1" long rings from 1" ID precision bore glass tubing, and setting these rings on glass slides. A hundred mounts can be cast in about two hours.

For subsequent polishing and etching procedures it is frequently desirable to make electrical contact with the back of the specimen in the mount. One simple way of doing this is to drill a hole through the back of the mount into the specimen and fill the hole with Woods Metal; contact is then made through this plug. Unfortunately, most of the alloyed specimens are so hard that they cannot be drilled. To handle the hard specimens, small cups were spun from soft copper. These cups are filled with molten solder; the metal piece pressed into the hot solder, and the whole molded in a metallographic

* This material is available from the Vernon Benshoff Company, P. O. Box 350, Albany 1, New York.

mount. A hole is drilled through the back of the specimen into the solder and a brass screw completes the contact.

Removal of the specimens from the Kold Mountings is accomplished by heating the mounts in glycerin to 150°C at which temperature the plastic becomes rubbery and the specimens fall out.

For many years no other means of preparing specimens was known except to polish on metallographic polishing wheels using conventional abrasives. For these procedures either the usual wet abrasives, or diamond abrasives were employed. In both cases preliminary grinding was by hand on either dry metallographic emery papers or wet silicon carbide papers, finishing on 600 grit or 3/0 papers. The material grinds slowly, and the deeply damaged layers from the cutting process are very difficult to remove. About forty minutes is required to grind and polish a specimen by these methods and the resulting finish is usually poor.

The equipment for "Automet Polishing" is the Buehler No. 1900AB Automet Polisher attachment. This is merely a mechanical lapping device in which specimens are clamped in holders, and all the equivalents of conventional grinding, polishing and finishing are mechanically performed. These attachments are capable of every variation of technique which would be used in conventional hand polishing. They are also capable of grinding under very heavy pressures, making them valuable for difficult materials. Since it is not necessary to touch the specimens or their holders while polishing, the Automets also lend themselves well to the etch polishing technique.

Etch-polishing is a procedure consisting of adding an etchant to the abrasive during the final stages of polishing. It is a procedure which has been used by metallographers for many years. When hand polishing methods are employed it is dangerous to use strongly corrosive etchants because of the likelihood of injury to the technician. With the automatic polishing attachments it becomes feasible to use any desired etchant. The etchant and abrasive combine in their action to remove the last vestiges of disturbed surface layers, leaving a clean, scratch-free specimen. The use of etchants for any except the finishing stages of polishing is unnecessary.

The process called "electro-mechanical polishing" is described in Metals Progress, October, 1958, pp. 142-144. In this process a weak current is passed through the specimen-polishing cloth interface and a mixture of abrasive and suitable electrolyte is used on the cloth. For it to succeed a number of variables must be carefully controlled. These include the wetness of the wheel, amount of abrasive, concentration and nature of the ion forming the electrolyte, voltage and polarity of the emf., pressure of the specimen on the cloth, and intensity of the current. Up to now it has been necessary to hold the specimens by hand so electrolytes were limited to those which would not injure the skin of the operator, and which would not form explosive or incendiary deposits with fine particles of metal or mounting material.

Both tantalum and tungsten can be electropolished and procedures for these operations have been known for several years. The high standards of quality which have been required in the refractory metals project has ruled out any attempt to produce specimens for the project by this means although some experimental work has been carried out along these lines.

The Preparation and Etching of Tantalum Specimens. Pure tantalum is soft, ductile and easily cold worked. Unless great care is exercised in preparation, the resulting microstructures will be characterized by scratches and other artifacts. The difficulties experienced in grinding a metal (metal removal) do not seem to have much relation to its hardness. Even though they are much harder, alloyed or strongly cold worked specimens of tantalum are more easily prepared than the pure soft metal.

Tantalum specimens can be prepared by conventional metallographic grinding and polishing procedures; however, these require a very long time. The use of a suitable etchant at the finishing stage greatly facilitates the production of soft specimens, but is not necessary for hard alloys.

The grinding steps prior to polishing tantalum are the same as those required for all moderately hard materials. Every effort must be made to insure that the remaining damaged layers are thin and that all prior damage is removed early in the process. Each grinding state should embody extremely

effective cutting action with good lubrication; dragging and slurry type abrasive must be avoided. Polishing wheels should be lightly charged, and used with a minimum of fluid and with very heavy pressure. The use of extremely heavy pressure not only helps to avoid relief effects but also aids in the retention of inclusions.

Where sufficient work is being done to warrant their cost, Automet polishing devices seem to provide the best method of preparing tantalum specimens. If possible, specimens for Automet polishing should be segregated and specimens of similar compositions and structure polished together. The sequence for the Automet polishing of tantalum specimens is as follows:

Steps	Abrasive	Time-minutes	Pressure-pounds	Lubricant
1	120 SiC	5	50	Water
2	120 SiC	5	50	Water(1)
3	240 SiC	5	50	Water
4	400 SiC	5	40	Water
5	600 SiC	5	40	Water
6	600 SiC	6	40-20	Water(2)
7	6 μ diamond	8	40	Kerosene
8	Linde B	4	50-20	Etchant--H_2O(3,4)

(1) The additional 120 SiC step is used to remove deeply damaged layers resulting from sectioning. It is not necessary with the harder alloyed specimens.

(2) The additional 600 SiC step is used to remove damaged layers from the previous grinding steps. It is used at 40 pounds pressure for the first two minutes followed by 20 pounds for about four minutes. It is continued until all deep scratches are removed and the specimen appears to be evenly ground. It is not required if the alloy is hard.

(3) Etchant composition

Dist. Water	275 ml *
Linde B	75 gm
Chromic Acid	5 gm

Whether or not an etchant is used with the Automet process the specimens should come off the wheels clean and bright, free from scratches and with a minimum of relief effects.

So far, no successful method has been worked out for using electromechanical polishing for the preparation of pure or high tantalum specimens.

Some attempts have been made to use electropolishing for preparing specimens of tantalum. The pure metal and single phase alloys can be electropolished without difficulty but the area which can be polished with present facilities is limited and the results obtained by electropolishing have not been considered acceptable. The following formulas are the ones which have been tried with tantalum.

1. Methanol 550 ml
   Sulfuric Acid 450 ml
   Voltage 20-30 time 10-30 sec.

2. Sulfuric Acid 90 ml
   Hydrofluoric Acid 10 ml
   Voltage 12-20 time 2-10 min.
   Voltage 1.5 time 3-10 sec.(1)

   (1) This procedure is used for brightening and removal of superficial layers from nearly perfectly polished specimens.

3. Water 40 ml
   Chromic Acid (CrO_3) 16 gm
   Hydrofluoric Acid 16 ml
   Sulfuric Acid 40 ml
   Voltage 6 time 10-30 sec.

* This is a modification of a procedure recommended in, DMIC Memorandum 37, Battelle Memorial Institute, Oct. 26, 1959.

4.	Water	350 ml
	Hydrofluoric Acid	100 ml
	Nitric Acid	100 ml
	Voltage 2-6	Current density 0.20-0.15 A/dm^2 Time to 5 min.

Tantalum can sometimes be chemically polished or brightened in one of the following formulas. This process has been erratic in its application and the results are usually unsatisfactory for microscopy.

1.	Acetic Acid	20 ml
	Sulfuric Acid	50 ml
	Hydrofluoric Acid	10 ml
2.	Lactic Acid	50 ml
	Nitric Acid	30 ml
	Hydrofluoric Acid	2 ml
3.	Nitric Acid	20 ml
	Hydrofluoric Acid	20 ml
	Sulfuric Acid	50 ml

The time with all these formulas is about 5-10 sec. and the solutions are used at about 20°C.

A number of etchants for tantalum are listed in various sources. The following formulas have been tried in this laboratory.

1.	Ammonium Fluoride	10 gm
	Water	50 ml
	Hydrofluoric Acid	50 ml
	Immerse 1 min. at 60°C	
2.	Ammonium Fluoride	2 gm
	Water	10 ml
	Sulfuric Acid	20 ml
	Immerse 1-2 min. at 60°C	

3. Ammonium Fluoride 2 gm
Water 10 ml
Nitric Acid 10 ml

Immerse at 60°C. Darkens Ta_2S_5

4. Ammonium Fluoride 20 gm
Water 100 ml

Immerse 5-6 min. 80°C. Develops grain structure without attacking Ta_2S_5.

5. Ammonium Fluoride 4 gm
Water 20 ml
Hydrogen Peroxide (3%) 10 ml

Use boiling. Colors Ta_2S_5 but does not attack the matrix.

None of the five preceding formulas containing Ammonium Fluoride have been satisfactory for general work due to their propensity for forming stains.

6. Hydrofluoric Acid 30 ml
Nitric Acid 15 ml
Hydrochloric Acid 30 ml

Use cold-Swab. Likely to be too vigorous.

7. Ortho phosphoric Acid 25 ml
Hydrofluoric Acid 20 ml
Nitric Acid 5 ml

Use cold-Swab. Useful etchant

8. Glycerol 75 ml
Hydrofluoric Acid 15 ml
Nitric Acid 10 ml
Hydrochloric Acid 15 ml

Use cold-Swab. Decomposes on standing. Delicate etch for Phases.

9. Glycerol 30 ml
Nitric Acid 30 ml
Hydrofluoric Acid 30 ml

Use cold-Swab. Very useful etchant. Decomposes on standing.

10. Lactic Acid 50 ml
Nitric Acid 10 ml
Hydrofluoric Acid 10 ml

Use cold-Swab. Useful where etch pits are troublesome.

11. Lactic Acid 50 ml
Nitric Acid 2 ml
Hydrofluoric Acid 3 ml

Use cold-Swab. Useful where reactive phases are troublesome.

12. Acetic Acid 50 ml
Nitric Acid 50 ml
Hydrofluoric Acid 10 ml

Use cold-Swab. Useful with cast alloys where coring is troublesome.

13. Hydrogen Peroxide (30%) 40 ml
Ethanol 8 ml
Nitric Acid 10 ml
Hydrofluoric Acid 10 ml

Use cold-Swab. Useful with some tantalum alloys. Explodes on standing. Do not keep more than 1 hour. Use carefully.

14. Lactic Acid 50 ml
Nitric Acid 3 ml
Hydrofluoric Acid 2 drops

Immerse cold. Do not swab. Very delicate etch for sensitive phases.

No etchants are known for tantalum which do not depend on the fluoride ion for their attack. Stains are common, but they can be sometimes removed by immersion in 50% hydrochloric acid in water or 10% hydrochloric acid in alcohol, or by 2-5 sec. repolishing on a finish wheel.

The Preparation and Etching of Tungsten and Tungsten Alloys. Tungsten resembles tantalum in its general behavior on grinding; however, it does not have as great a tendency to form damaged surface layers. It is generally much harder than tantalum, and the specimens are likely to be brittle. It grinds exceedingly slowly and has a great tendency to show relief effects and pitting unless carefully prepared.

Tungsten specimens can be fairly easily prepared by conventional metallographic processes using wet wheels, or even better results can be obtained with diamond wheels. In all cases heavy pressure and effective cutting action are essential. Where wet polishing is done the specimens will finish more easily if an etchant is used at the finish stage. A suitable etchant has the following composition.

Water	150 ml
Potassium Ferricyanide	3.5 gm
Potassium Hydroxide	1 gm

The Automet polishing process provides an improvement over the conventional or hand method of preparing tungsten specimens. It is also a very suitable method of preparing specimens for subsequent finishing by the electro-mechanical or electropolishing process. The same sequence of operations on the Automet given for tantalum is also suited for tungsten up to the finishing step. The finishing step must be handled differently.

Specimens can be finished on the Automet either with or without an etchant. If an etchant is to be used, the one given for hand polishing is satisfactory; however, it must be used only for a very short time (1-2 minutes) or severe relief effects will result. Tungsten specimens can also be finished on the Automets substituting a one micron diamond wheel for the Linde A & B wheel. The time on this diamond wheel is about 6-8 minutes or until a good polish is obtained. To avoid relief effects care should be taken not to polish longer than necessary.

The most effective way of finishing tungsten specimens has been by the electro-mechanical method. In this process the specimens are ground and finished as well as possible in the Automet without using any etchant. Any fine scratches left on the specimen will be removed by the electro-mechanical step.

The power supply for the electro-mechanical process is a rectifier device which will provide a potential of from 4-8 volts in such a way that the specimen is cathodic about 75% of the time and anodic the remainder.

The voltage is oscillated about 100 times per minute. Connection is made to the back of the specimen using a flexible lead and a small battery clip. The method of making this contact is described in the paragraphs on mounting of specimens.

The wheel is covered with a soft napped wool cloth (Miracloth) or a synthetic cloth such as Gamal or Microcloth. The abrasive, Linde B, is applied by means of a salt shaker. The electrolyte consists of about 30 gm of potassium ferricyanide in 100 ml of distilled water. It is applied from an Erlenmeyer flask with a shaker top. Another shaker top flask filled with distilled water is also necessary. The ferricyanide solution is applied to the wheel at a ratio of about 1 part to 10 parts distilled water. The abrasive is used generously. The wheel is used very wet and with a pronounced slurry at a rotational speed of about 160 rpm. The specimen is floated on the wheel with a very light pressure so that a current of approximately 250 μA passes through it. The time for finishing by this method may range from about 30 sec. to 3 min. The specimens should come off clean and bright, unetched and free from scratches. When properly done the results by this process are very beautiful. Although the process sounds complicated, it is rather quickly learned. It works well with compositions from 40% tungsten up to pure tungsten. The ferricyanide solution does not seriously attack the skin but may cause some blackish stain with protracted use. Although it is somewhat poisonous it is not dangerous if precautions are taken against getting it in the mouth or on mucous membranes.

Tungsten and single phase tungsten alloys can be readily electropolished in a number of electrolytes. The quality of the electropolished specimen, however, reflects the care which has gone into its prior preparation. This being the case, it is generally easier to finish a specimen by other than electrolytic means since the results are usually better. The following electrolytes have been successfully used.

1.	Water	1000 ml
	Sodium Hydroxide	100 gm
	Voltage 6	Time 5-30 min.

2. Water 1000 ml
Tri-Sodium-Phosphate 160 gm
Voltage 2-6 Time 1/2 - 10 min.

The etching of tungsten and tungsten alloys is somewhat difficult. The pure metal is slowly soluble in a mixture of hydrofluoric and nitric acids, but the usual result of this treatment is severe etch pitting. It is also very slightly attacked by a mixture of nitric and sulfuric acids. Due to its tendency to pit, however, the most successful etchants are those which delineate grains and grain boundaries by the formation of films. The following etchants have been used with varying degrees of success.

1. Water 40 ml
Nitric Acid 10 ml
Hydrofluoric Acid 30 ml

Used hot this solution will rapidly develop etch pits. Cold it will sometimes satisfactorily etch certain alloys.

2. Water 100 ml
Potassium Ferricyanide 10 ml
Potassium Hydroxide 10 ml

Etch by immersion. Do not swab.

3. Water 150 ml
Potassium Ferricyanide 3.5 gm
Sodium Hydroxide 1 gm

Etch by immersion or swabbing

4. Water 100 ml
Potassium Ferricyanide 30 gm
Sodium Hydroxide 5 gm

Used for etch pitting single crystals and for orientation studies.

5. Hydrofluoric Acid 10 ml
Nitric Acid 10 ml
Ethanol 8 ml
Hydrogen Peroxide (30%) 30 ml
Potassium Ferricyanide 15 gm

Unstable and explosive. The final composition of this etchant is uncertain. Its action is erratic.

6. Hydrogen Peroxide (30%)

   Use cold by swabbing or slightly warmed.

7. Hydrogen Peroxide (3%)

   Use cold on delicate alloys or boiling on pure metal.

8.

Lactic Acid	50 ml
Nitric Acid	10 ml
Hydrofluoric Acid	10 ml

   This reagent gives a slight chemical polishing action and very clean microstructures. It has been used on most of the recent work.

All of the above etchants, with the exception of Nos. 1 and 8, are film formers. Under certain conditions these films can be removed in solutions of hydrochloric acid in water or alcohol.

Tungsten can also be etched electrolytically in one of the following solutions. Voltage and current density are usually critical and have to be determined for each case.

9.

Water	25 ml
Sodium Hydroxide	1 gm
Hydrogen Peroxide (3%)	25 ml

10.

Water	50 ml
Sodium Hydroxide	1 gm

   Current density 5 A/dm^2

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APPENDIX C

ANALYTICAL PROCEDURES FOR TANTALUM, TUNGSTEN AND THEIR ALLOYS

by

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Tungsten-Tantalum-Rhenium - A survey of the literature revealed no method for the separation and determination of these three elements when present together. The analysis is complicated by the fact that tungsten and tantalum form simple water-soluble salts only in alkaline or fluoride solution.

However, this acid insolubility may be used to separate tantalum and/or tungsten from rhenium. There is no loss of rhenium due to co-precipitation even though only a few per cent may be present.

Rhenium may be precipitated with tetraphenylarsonium chloride[6] or nitron[2]. The former reagent, first recommended by Willard and Smith[6] and modified by Smith and Long[5], was chosen because there are fewer interferences. Willard and Smith[6] stated that moderate amounts of nitrates interfere. This work shows that up to nine grams of ammonium nitrate may be present in 100 ml. of solution. Cinchonine, hydrogen peroxide, tungstates, alkali, or acid do not interfere, but tantalum does.

At least 10 mg. of rhenium may be quantitatively separated as the sulfide without using a pressure vessel, which is recommended by Geilmann[1]. Tantalum may be complexed as fluoride.

Powell, Schoeller, and Jahn[3] suggested that tantalum may be separated from tungsten by precipitation with magnesium chloride solution. This separation was found to be satisfactory.

Experimental

Reagents

1. Potassium carbonate, 1% W/W in water.
2. Magnesium chloride, 10% W/W in water.
3. Cinchonine, 10% W/W in hydrochloric acid (6 N).
4. Hydrogen peroxide, 30%.
5. Tetraphenylarsonium chloride, 1% in water.
6. Tetraphenylarsonium perrhenate, saturated solution in water for washing.
7. Hydrogen sulfide gas.

Procedure for Ternary Alloys

High Rhenium. Dissolve about 0.2 g. of sample in 20 ml. of 6 N hydrochloric acid plus 5 ml. of hydrogen peroxide. Dilute to 100 ml. and add 10 ml. of cinchonine solution and 5 ml. of nitric acid. Boil till the peroxide is decomposed, and set aside overnight at room temperature. Filter through No. 42 Whatman paper. Save the filtrate which contains the rhenium.

Ignite the paper containing tantalum and tungsten in a platinum crucible till the paper is burned away. Add five grams of anhydrous potassium carbonate and fuse till clear. Cool and dissolve the melt in 50 ml. of cold water. Rinse off the crucible, and add 10 ml. of magnesium chloride solution. Stir and heat to about 90°C. Let cool for 30 minutes, and filter the magnesium tantalate precipitate on No. 40 Whatman paper. Wash with 1% potassium carbonate solution.

Acidify the filtrate with hydrochloric acid and add a 10 ml. excess. Boil out the carbon dioxide, and add 5 ml. of nitric acid and 10 ml. of cinchonine solution. Allow to sit overnight at room temperature. Filter through No. 42 Whatman paper and ignite to WO_3 in an electric muffle at 800°C.

The paper and precipitate of magnesium tantalate are treated with hydrochloric acid (1 N). Neutralize with ammonia, but leave enough free acid to keep the cinchonine in solution. Heat and add a 50% excess of tetraphenylarsonium chloride. Let sit overnight at room temperature. Filter through a weighed porous porcelain crucible. Wash and transfer the precipitate with saturated tetraphenylarsonium perrhenate solution. Dry at 110°C and weigh as $(C_6H_5)_4AsReO_4$.

Low Rhenium Alloys. If the weight of the rhenium is less than 10 mg. and tantalum is present, the rhenium is best separated as the sulfide. Dissolve the sample in a platinum crucible with 2 ml. of hydrofluoric acid plus a few drops of nitric acid. Heat to drive out nitrous fumes. Transfer to a pyrex beaker containing 100 ml. of water and one gram of tartaric acid to complex tungsten, if present. Saturate with hydrogen sulfide. Heat to boiling and saturate again with hydrogen sulfide. Let sit overnight

at room temperature. Filter through medium porosity paper, and wash with water saturated with hydrogen sulfide. Saturate the filtrate with hydrogen sulfide and heat again. If more precipitate forms, filter through the same paper. Dissolve the sulfide by pouring a solution containing 50 ml. of ammonium hydroxide (7 N) and 10 ml. of hydrogen peroxide, and add tetraphenylarsonium chloride to the ammoniacal solution.

Binary Alloys

If only tantalum and tungsten are present or if rhenium was determinted in a separate sample, the sample may be oxidized in a platinum crucible over a Fisher burner. The oxides are ready for fusion with potassium carbonate.

Rhenium and tungsten do not interfere with each other. Rhenium may be precipitated directly in dilute alkaline solution. Tungsten may be precipitated with cinchonine in dilute acid solution.

Volatile rhenium oxide is lost upon ignition. In binary alloys a simple ignition at 800°C will give a rough idea of the amount of rhenium present.(7)

Results and Discussion

Known amounts of two or all three of the pure metals, totaling 0.2 g., were mixed and carried through the procedure. The results are shown in Table I to V.

Schoeller's(3) magnesia separation of tantalum from tungsten was found to yield quantitative separation (Tables I and II). Each oxide was examined spectrographically and found to contain less than 0.1% of the other oxide.

Up to at least ten milligrams of rhenium may be recovered as sulfide without the use of a Geilmann(1) pressure vessel (Table III). The final precipitation as tetraphenylarsonium perrhenate was made in the presence of ammonium hydroxide and hydrogen peroxide, so these are shown not to interfere.

TABLE I

Ta-W, Determination of Tungsten

W added, mg.	W found	Error
2.9	3.1	+ 0.2
19.6	19.9	+ 0.3
47.5	48.1	+ 0.6
71.8	71.1	- 0.7
84.6	83.3	- 1.3
95.8	96.2	+ 0.4
96.5	96.7	+ 0.2
118.9	117.6	- 1.3
176.1	176.4	+ 0.3
183.8	184.5	+ 0.7

TABLE II

Ta-W, Determination of Tantalum

Ta added, mg.	Ta found	Error
21.2	21.6	+ 0.4
56.7	56.7	0
82.8	82.6	- 0.2
100.3	100.2	- 0.1
102.8	101.8	- 1.0
122.0	120.8	- 1.2
150.2	151.9	+ 1.7
179.0	180.6	+ 1.6

TABLE III

Rhenium after Sulfide Separation

Re added, mg.	Re found	Error
1.8	1.9	+ 0.1
2.0	1.9	- 0.1
10.0	10.1	+ 0.1
13.1	12.8	- 0.3
52.6	51.6	- 1.0
100.3	99.4	- 0.9
101.6	100.7	- 0.9

TABLE IV

Rhenium Directly, Tantalum Absent

Re added, mg.	Re found	Error
12.7	12.7	0
22.9	23.0	+ 0.1
63.0	63.4	+ 0.4
80.2	81.1	+ 0.9
101.6	101.3	- 0.3

TABLE V

Ternary Alloys, Data in Milligrams

Tantalum A			Tungsten B			Rhenium C		
Added	Found	Error	Added	Found	Error	Added	Found	Error
101.3	102.8	+ 1.5	46.0	45.9	- 0.1	55.0	54.8	- 0.2
53.6	53.6	0	87.1	87.0	- 0.1	49.6	50.0	+ 0.4
154.2	154.2	0	79.9	79.3	- 0.6	26.0	24.7	- 1.3
90.9	92.3	+ 1.4	21.6	20.7	- 0.9	92.0	92.1	+ 0.1
20.1	20.1	0	167.6	168.8	+ 1.2	10.4	10.3	- 0.1
151.4	154.1	+ 2.7	24.6	24.3	- 0.3	31.6	32.1	+ 0.5
39.7	39.6	- 0.1	37.4	38.5	+ 1.1	121.1	120.5	- 0.6
10.4	10.6	+ 0.2	180.9	179.1	- 1.8	9.9	10.0	+ 0.1
3.2	3.4	+ 0.2	196.0	194.6	- 1.4	1.9	1.4	- 0.5
191.1	193.3	+ 2.2	1.4	0.3	- 1.1	1.9	1.5	- 0.4

TABLE VI

Statistical Data for y = bx

Table	System	Slope, b	90% Confidence Interval	s.d.
I	W in W-Ta	1.00	0.99 - 1.01	0.80
II	Ta in W-Ta	1.00	0.99 - 1.01	1.05
III	Re after H_2S	0.99	0.98 - 1.00	0.26
IV	Re in W-Re	1.00	0.99 - 1.01	0.52
Va	Ta in Ta-W-Re	1.01	1.00 - 1.02	0.78
Vb	W in Ta-W-Re	1.00	0.99 - 1.01	1.03
Vc	Re in Ta-W-Re	1.00	0.99 - 1.01	0.56

Table IV shows that rhenium may be precipitated in the presence of sodium hydroxide and tungstate without interference. Tantalum precipitates even in the presence of fluoride or tartrate.

In Table V rhenium was determined after the separation of tungstic and tantalic acids. These acid insoluble elements did not co-precipitate significant quantities of rhenium. When the rhenium was precipitated, about nine grams of ammonium nitrate and one gram of cinchonine were present. Neither of these interferred with the rhenium determination.

The data in these tables were analyzed statistically by using the model, $y = a + bx$. The milligrams added is represented by x, and the milligrams found by y. The intercept is a, and b is the slope. In no case was the intercept or blank found to be significantly different from zero (90% confidence level). Consequently the model, $y = bx$, was adopted. The data, along with the standard deviations, are shown in Table VI. A value of 1 for the slope represents quantitative recovery. From these data it is clear that in all cases the respective methods may be considered satisfactory.

In only two cases does the slope differ from one. Table III shows that more than 10 mg. of rhenium may not be completely precipitated with hydrogen sulfide. In this case rhenium may be determined in the filtrate from tantalic and tungstic acids. Results for large amounts of tantalum (Table Va) may be high. In this case perhaps tantalum is better calculated by difference. The last figure in Table Vb suggests that milligram amounts of tungsten are not completely recovered. Therefore, a colorimetric method such as Short's dithiol[4] method is recommended for small amounts of tungsten.

Tantalum-Zirconium - The problem is mainly one of separation. Tantalum interferes in practically all of the methods for the determination of zirconium.

The organic precipitating agents for zirconium, such as mandelic acid,[10] also precipitate tantalum either directly or by hydrolysis.

Niobium may be separated from zirconium after fusion with potassium carbonate.[8] For tantalum the fusion separation is far from satisfactory.

Milner and Barnett[11] separated zirconium in hydrofluoric acid solution as barium fluozirconate. Tantalum is listed as one of the non-interferring elements, but when 0.2 g. samples are used, considerable tantalum precipitates with the zirconium.

Tantalum must be separated before zirconium can be titrated with EDTA[11,12] as tantalum also forms a weak complex with the reagent.

Milner and Edwards[12] found that tantalum could be extracted with methyl-isobutyl ketone from hydrofluoric-sulfuric acid solution. However, in this laboratory, some zirconium was also extracted unless the amount of hydrofluoric acid was reduced below the suggested 4 ml. per 25 ml. of solution. The results were satisfactory when 3 ml. of hydrofluoric acid were used, but erratic when only 2 ml. were used.

The procedure was also simplified. After the solution of the sample the evaporation to fumes of sulfuric acid was eliminated. The use of the "conditioned" ketone was found to be unnecessary.

The extraction of tantalum was not quite complete in one extraction. The few milligrams of tantalum left remained soluble while the zirconium was precipitated with ammonia in the presence of hydrogen peroxide. The zirconium was then ignited to the oxide.

A gravimetric finish was desired because sometimes both zirconium and hafnium were present. The zirconium-hafnium ratio was determined spectrographically in the mixed oxide precipitate. However, the given procedure is not quantitative for hafnium. From ten to twenty percent of the hafnium was extracted by the ketone along with the tantalum.

Experimental

Apparatus and Reagents

Polyethylene separatory funnel. This may be made as described by Milner and Edwards.[12]

Methyl-isobutyl ketone.

Ammonium nitrate wash solution, 3% W/V.

Hydrogen peroxide, 30%.

Procedure

Weigh 0.2 g. of sample (enough to contain between 2 and 20 mg. of zirconium) into a platinum dish. Moisten with 0.2 ml. of sulfuric acid (18 N) to prevent volatilization of zirconium. Add 3 ml. of concentrated hydrofluoric acid. Cover the dish as action may be vigorous. Complete solution by adding nitric acid, a few drops at a time. Place on a hot plate long enough to drive out oxides of nitrogen.

Transfer to a plastic separatory funnel with the help of 16 ml. of sulfuric acid (18 N) and 6 ml. of water. Add 25 ml. of methyl-isobutyl ketone and shake thoroughly. Allow the layers to separate and draw off the lower (acid) layer into the original platinum dish.

Evaporate to light fumes of sulfuric acid. Cool and wash down the sides of the dish with water. Evaporate again to fumes of sulfuric acid and continue fuming for five minutes. A little carbon will remain on the sides of the dish, but this contains no zirconium and may be neglected.

Cool and transfer the solution to a Pyrex beaker. Add 5 ml. of 30% hydrogen peroxide and dilute to 100 ml. with water. Add ammonium hydroxide till the solution is neutral to methyl red, then a 0.5 ml. excess. Heat to 90°C. Add paper pulp and filter through No. 40 Whatman paper. Wash with 3% ammonium nitrate solution. Ignite in platinum over a Fisher burner and weigh as ZrO_2.

For accurate work a blank should be run on the reagents and the precipitate checked for impurities.

Results and Discussion

Accuracy and Precision

Known amounts of pure zirconium and tantalum were weighed and carried through the entire procedure. The results for zirconium are listed in Table VII.

The data were analyzed statistically as described by Youden[13] and fitted to the equation $y = a + bx$. The intercept or blank is a, and the slope, (ideally one), is b. The amount of zirconium taken is x, and

TABLE VII

Zirconium in Tantalum

Use 0.2 g. Samples

Zr added, mg.	Zr found	Error
2.0	1.9	- 0.1
3.0	2.8	- 0.2
5.0	4.6	- 0.4
8.1	8.7	+ 0.6
8.6	8.1	- 0.5
10.1	10.4	+ 0.3
15.1	14.3	- 0.8
20.2	20.5	+ 0.3
20.8	20.5	- 0.3
38.9	39.8	+ 0.9

the amount found is y. The value for a is -0.33 mg with the 95% confidence interval between -0.90 and +0.25 mg. The value for b is 1.02 with a 95% confidence interval between 0.98 and 1.06. The standard deviation for a single determination is 0.49 mg. or 0.25% for a 0.2 g. sample. On this basis the determination is accurate within the precision.

Completeness of Separation

Only one extraction may be made or some zirconium may be lost. About five milligrams of tantalum remain unextracted. This amount of tantalum was found to be completely separated with one ammonia-peroxide precipitation of zirconium. Within the limits of reading an analytical balance, the results for single and double precipitations were the same. The zirconium oxide precipitates were analyzed spectrographically and contain less than 1% tantalum.

Interferences

Only the related metals titanium and niobium were investigated. Titanium remains in the acid layer after the extraction and is precipitated with ammonia even in the presence of peroxide. If titanium is present, fuse the zirconium oxide with potassium bisulfate and determine the titanium colorimetrically with hydrogen peroxide.

Moderate amounts of niobium do not interfere. It is extracted with the ketone not quite as completely as tantalum. The remainder of the niobium is complexed with peroxide while the zirconium precipitates with ammonia.

Many metals such as aluminum and iron precipitate with ammonia. In more complicated alloys zirconium and hafnium may be precipitated as phosphate from 3.6 N sulfuric acid after the tantalum is removed by extraction. Peroxide is used to complex the few milligrams of unextracted tantalum and titanium, if present. The procedure is described by Hillebrand and Lundell.(9)

Hafnium Recovery

Generally zirconium and hafnium behave alike in analytical reactions. In this case the recovery of hafnium is only 80 to 90% complete. The rest is extracted by the ketone along with the tantalum. Therefore, a suitable method for the determination of hafnium in tantalum must still be found.

Oxygen Determination - Oxygen is determined in rhenium, hafnium, tungsten and tantalum, and their alloys, by vacuum fusion. Alloys containing Re, Hf, Ta and small amounts of W are analyzed in a platinum bath at 1900°C. Tungsten-base alloys are analyzed in an iron-tin bath at 1700°C. The absolute accuracy of the method has never been determined for the metals under consideration although the precision of the measurements is within ± 10% of the amount of oxygen measured.

Nitrogen Determination - Nitrogen can be determined in Re, Hf and Ta, and alloys of these three metals, by the method previously developed for niobium. The samples are dissolved in HF and H_2O_2 and then the ammonia formed is steam distilled and titrated. When tungsten is present this method is not applicable. A digestion in H_2SO_4 must be used which, because of the length of time necessary, leads to a higher blank than with the HF digestion. The amount of nitrogen usually present in tungsten base alloys is so small that the blank can easily equal or surpass the amount being determined. In most cases, the determination of nitrogen in tungsten base alloys is an assay.

Tungsten-tantalum - The oxides are fused with potassium carbonate and the tantalum separated with magnesia. Then the tungsten is precipitated in acid solution with cinchonine. Tantalum is precipitated with ammonia after extraction of magnesium salts with acid.

Tantalum-hafnium - The alloy is dissolved in nitric and hydrofluoric acids. The hafnium is separated by double precipitation of barium-fluohafnate. The precipitate is dissolved in nitric and boric acids, an excess of a standard solution of ethylenedinitrillo - tetra-acetic acid (EDTA)(.01M). The excess EDTA is titrated with .01M ferric ferric ion solution. The

method is an adaptation of that of Milner and Barnett for the determination of zirconium in fluoride-containing solutions.

Tantalum-titanium - The sample is fused with potassium bisulfate and the titanium determined colorimetrically with hydrogen peroxide. Molybdenum and vanadium interfere, but these may be removed by fusion with potassium carbonate. In any case a fusion with potassium carbonate is recommended if the titanium content is less than one percent. The useful range is .01 to 20%. The standard deviation is .02% for vanadium and .04% for chromium.

Tantalum-molybdenum - Molybdenum is separated as the sulfide while tantalum is complexed with hydrofluoric acid. The sulfide is ignited to the oxide and weighed. The range is 0.5 to 20% while the standard deviation is .04%.

Tantalum-chromium and tantalum-vanadium - Either chromium or vanadium may be determined by oxidation with persulfate and titration with ferrous ammonium sulfate. Tantalum is kept in solution with hydrofluoric acid. The range is 0.5 to 50%. The standard deviation is .02% for vanadium and .04% for chromium.

Tungsten-titanium and tungsten-zirconium - Titanium and zirconium may be separated by precipitation with potassium hydroxide while the tungsten remains in solution. The titanium or zirconium may then be determined by any standard method. Only one set of samples was analyzed and the range was 0.25 to 15%. The precision was not determined.

Tungsten-vanadium and tungsten-chromium - Vanadium and chromium may be determined in tungsten the same as in steels or tantalum. Tungsten may precipitate during the persulfate oxidation, but causes no trouble except to make a visual end point harder to see. The precision was not determined.

Tungsten-molybdenum - Small amounts of molybdenum (about 0.1%) may be determined in tungsten colorimetrically with thiocyanate. No work has been done to determine larger amounts of Mo in tungsten.

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APPENDIX D

STUDIES IN THE TANTALUM-ZIRCONIUM SYSTEM

by

Allen I. Lewis

The influence of a single heat treatment, 16 hours at 2000°C followed by slow cooling (12 hours to reach room temperature), upon hardness and microstructure of Phase I and Phase III alloys was discussed in earlier portions of this report. Significant hardness increases upon annealing were observed for Ta base alloys containing Zr. Results were interesting enough to warrant further study.

Additional heat treatment of a Ta-8.4Zr alloy button indicated response typical of aging. The results of each sequential treatment are presented in Table I. Heat treatment varied the hardness of this alloy from a high of 558 to a low of 226 VHN. Corresponding changes in microstructure are shown in Figures 1 to 5.

Material for further evaluation was obtained from a Ta-8Zr non-consumably arc melted sheet bar, processed as part of the Phase II scale up program. The bar was reduced 66% in thickness by rolling to 125 mils at 1200°C. After removing a protective stainless steel can, the strip was ground an equal amount on each side to provide 50 mil stock. This sheet bar cracked during rolling. A Ta-4Zr alloy was made by consumable arc melting and was extruded successfully but laminated excessively during hot rolling to strip. These results were reported in earlier sections of this report. Typical microstructures after fabrication are shown in Figures 6 to 8. All alloys contain varying amounts of a precipitate phase, rod-like or peppery in form. Failure appears to be associated with this precipitate.

Typical as cast and annealed hardnesses for Ta-4Zr and Ta-8Zr 20 gram arc melted alloy buttons are shown in Table II, along with values for the "as fabricated" material. Annealing 16 hours at 2000°C increased the hardness of the 20 gram buttons. However, working had a minor influence upon the other heats since only the Ta-4Zr alloy, which had been extruded and rolled, increased significantly in hardness. Sufficient material was salvaged from Ta-8Zr sheet bar to permit a cursory study of the influence of heat treatment upon hardness and microstructure. The strip was analyzed and found to contain 6.27% Zr, 0.0190% O, and 0.084% C.

Specimens were solution treated between 1800°C and 2600°C. Quenching for most treatments was accomplished by turning off the furnace power, thus

TABLE I

EFFECT OF SEQUENTIAL HEAT TREATMENT UPON THE HARDNESS AND MICROSTRUCTURE OF A Ta-8.4Zr ALLOY

Treatment	Hardness
non-consumably arc melted	305
16 hours at 2000°C cooled slowly *	558
16 hours at 2200°C R.Q. **	462
72 hours at 1200°C cooled slowly	226
1 hour at 2200°C P.Q. ***	471

* Approximately 12 hours to reach room temperature

** Power turned off. Temperature dropped below black heat in approximately 2 minutes.

*** Dropped from hot zone onto a water cooled plate. Black in less than 30 seconds.

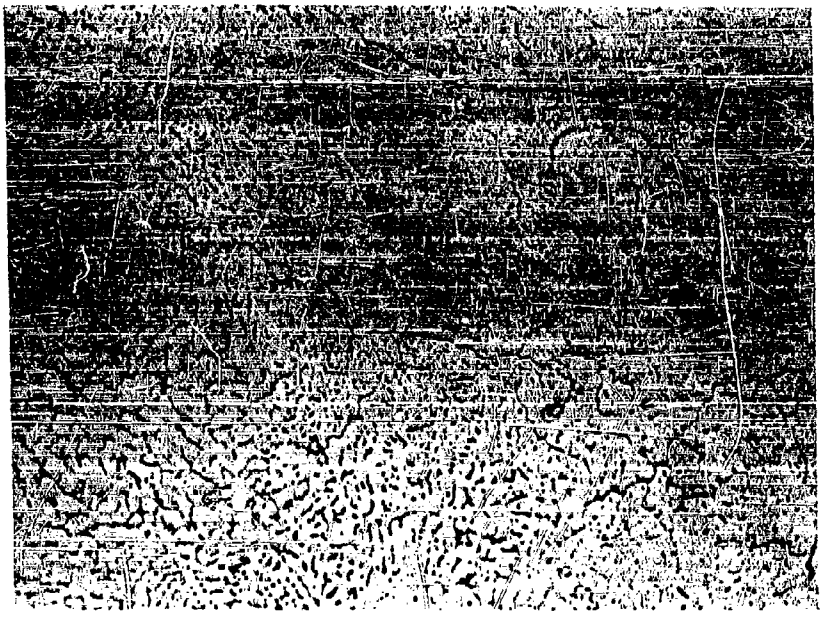

Fig. 1--Ta-8.4 Zr, as cast. 100X

Fig. 2--Ta-8.4 Zr, annealed 16 hours at 2000°C, slow cooled. 100X

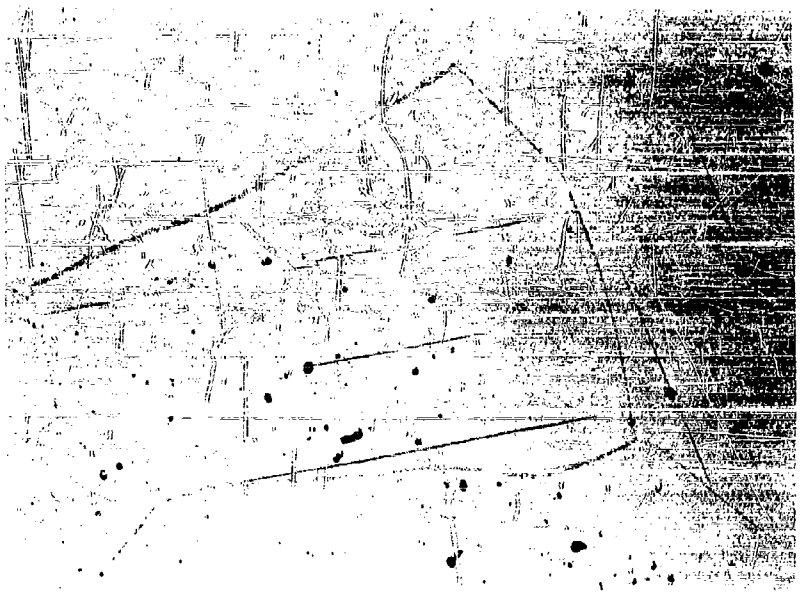

Fig. 3--Ta-8.4 Zr, annealed 16 hours at 2000°C, slow cooled; 16 hours at 2200°C, radiation quenched. 100X

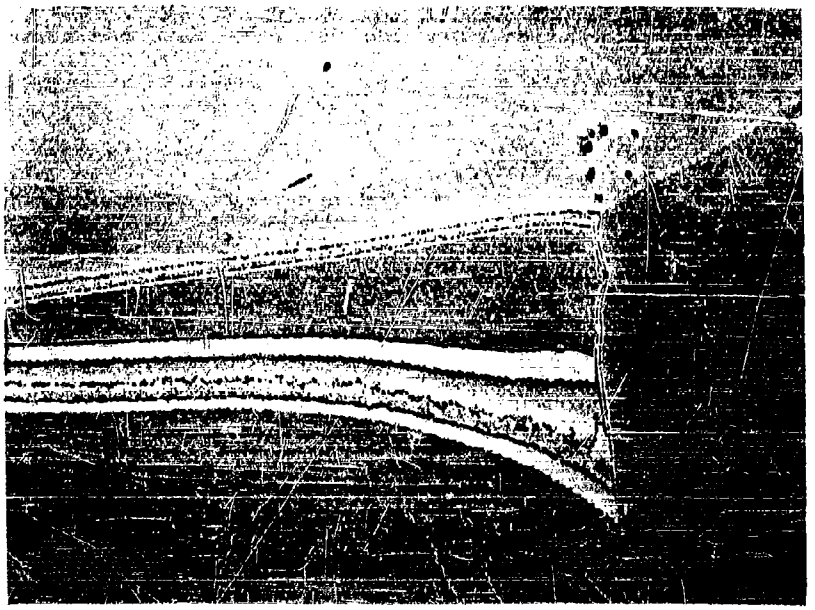

Fig. 4--Ta-8.4 Zr, annealed 16 hours at 2000°C, slow cooled; 16 hours at 2200°C, quenched; 72 hours at 1200°C, slow cooled. 100X

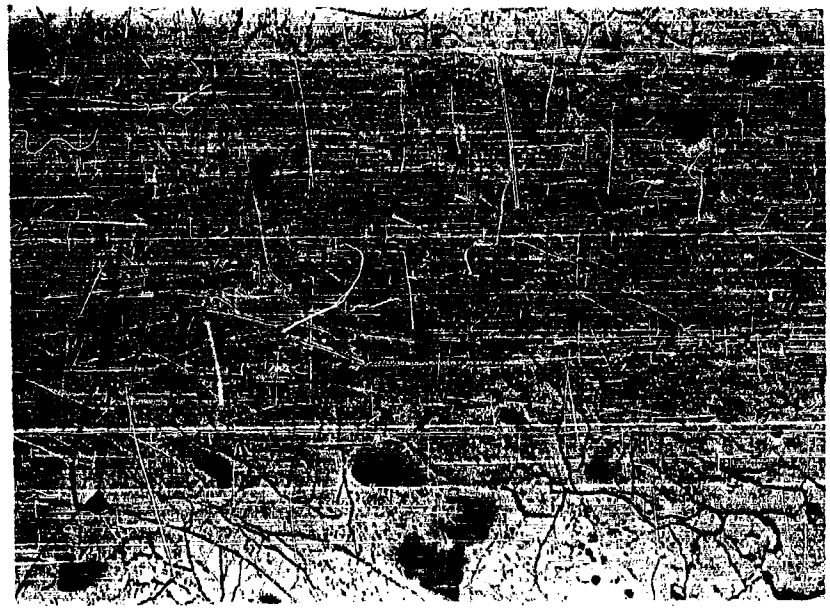

Fig. 5--Ta-8.4 Zr, annealed 16 hours at 2000°C, slow cooled; 16 hours at 2200°C, quenched; 72 hours at 1200°C, slow cooled; 1 hour at 2200°C, quenched.
100X

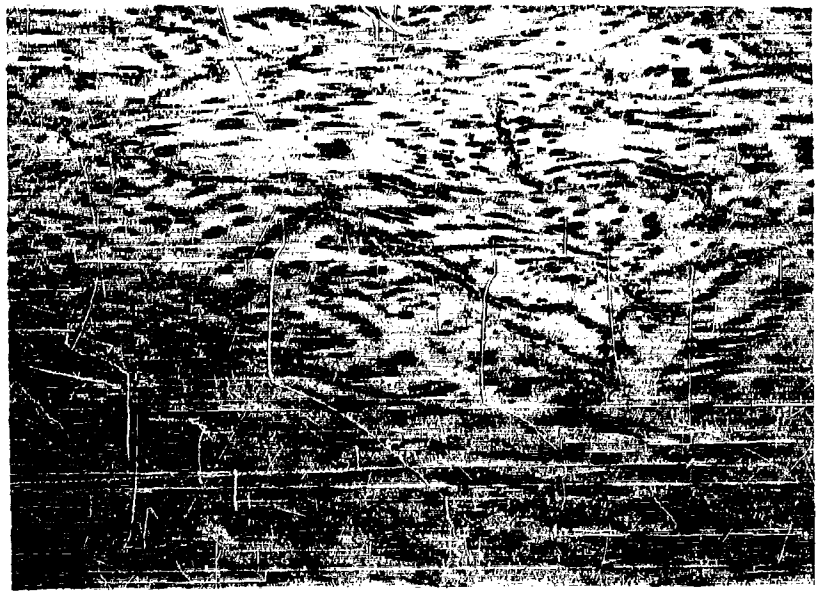

Fig. 6--Longitudinal section through Ta-4 Zr arc melted sheet bar after an unsuccessful attempt to roll at 1200°C.
100X

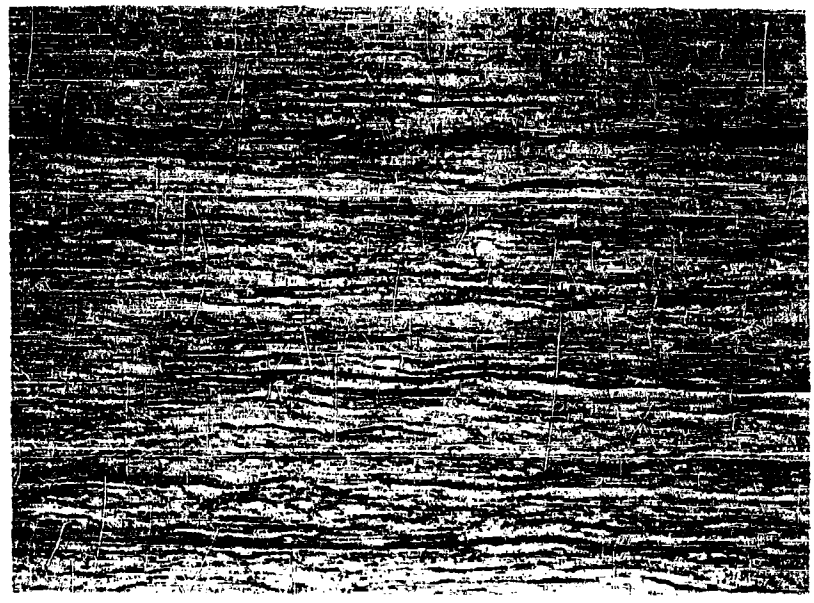

Fig. 7--Microstructure of a Ta-4 Zr alloy CAM billet. Dynapak extruded to sheet bar and rolled to 80 mil sheet at 1200°C 100X

Fig. 8--Microstructure of a Ta-8 Zr consumably arc melted billet which exploded during Dynapak extrusion. Billet was held 2 minutes at 1750°C, allowing the billet 7 minutes to reach temperature prior to extrusion. 100X

TABLE II

INFLUENCE OF TREATMENT UPON HARDNESS OF Ta-4%Zr and Ta-8%Zr ALLOYS

Composition	Method of Preparation	Condition	Hardness VHN
Ta-4%Zr	20 gram non-consumably arc melted button	arc melted	204
Ta-4%Zr	20 gram non-consumably arc melted button	arc melted, annealed 16 hrs. at 2000°C	267
Ta-4%Zr	150 gram non-consumably arc melted sheet bar	Hot rolled at 1200°C	235
Ta-4%Zr	Consumably arc melted billet	Dynapak extruded after heating at 1750°C. Hot rolled at 1200°C	309
Ta-8%Zr	20 gram non-consumably arc melted button	arc melted	305
Ta-8%Zr	20 gram non-consumably arc melted button	arc melted, annealed 16 hrs. at 2000°C	558
Ta-8%Zr	150 gram non-consumably arc melted sheet bar	Hot rolled at 1200°C	290
Ta-8%Zr	Consumably arc melted billet	Dynapak extruded Exploded during extrusion	305

allowing the specimen to radiate to black heat in less than three minutes. This procedure was termed radiation quenching. A more rapid technique termed pot quenching was achieved by dropping specimens out of the furnace hot zone, thereby cooling them to black heat almost instantly. The influence of solution treatment upon microstructure is shown in Figures 9 to 18. Generally, grain size increased with temperature and time at temperature. A lamellar grain boundary structure was present in all specimens. This structure decreased in amount with increasing temperature and time at temperature. Since grain growth was observed, precipitation at boundaries must have taken place during quenching. Figure 18 is a photomicrograph of a specimen showing melting at 2600°C.

To determine if the boundary structure could be suppressed, a specimen was pot quenched. The quantity of boundary structure was reduced slightly but not suppressed, as can be seen by comparing Figures 15 and 19.

The grain boundary structure was subjected to x-ray microprobe analyses at Advanced Metals Research Corporation. Figure 11 is a photomicrograph of the specimen chosen for analysis. After 15 minutes at 2000°C this specimen contained a boundary network sufficiently dense for study. Traverses were made across grain boundaries. The distribution of Ta and Zr across a typical boundary is shown in Fig. 20. The boundary structure was found to be depleted in Zr and enriched in Ta compared to the matrix, with Zr enrichment just outside the structure-matrix boundary. The analysis revealed a definite tendency for Zr to migrate from the boundaries into the matrix. Carbide precipitation of a phase depleted in Zr could account for this behavior, but attempts to obtain confirmation of this potulate by x-rays were unsuccessful.

Heat treatment had a moderate effect upon hardness, as shown in Table III. Annealing above 1800°C tended to raise hardness. 16 hours at 2000°C raised the hardness 120 VHN whereas 1 hour at 2200°C increased hardness over 60 VHN. One hour at 2400°C increased hardness only 30 VHN compared to the as worked alloy. Alloys were found to be softer at the edges due to Zr loss by evaporation during annealing. Tukon hardness traverses indicated that the grain boundary structure was considerably softer than the matrix,

Fig. 9--Ta-6.3 Zr, as rolled. 100X

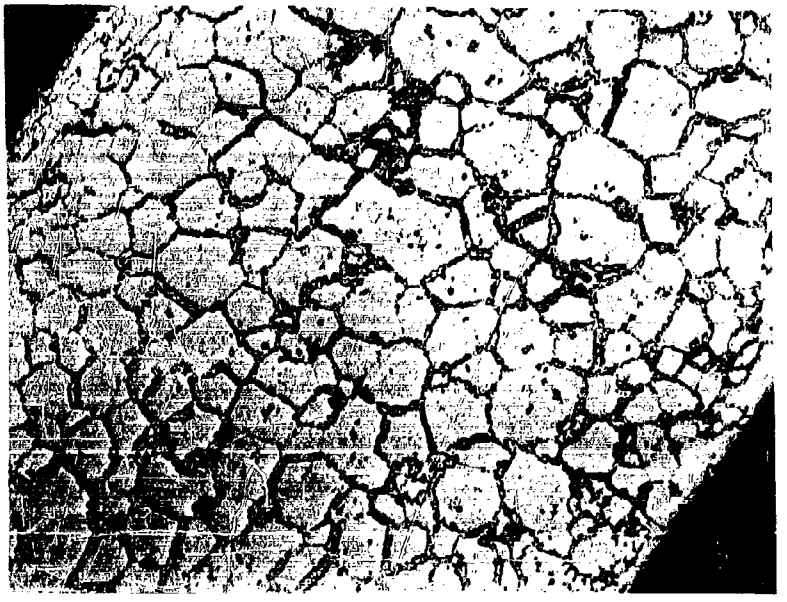

Fig. 10--Ta-6.3 Zr, 1 hour at 1800°C, radiation quenched. 100X

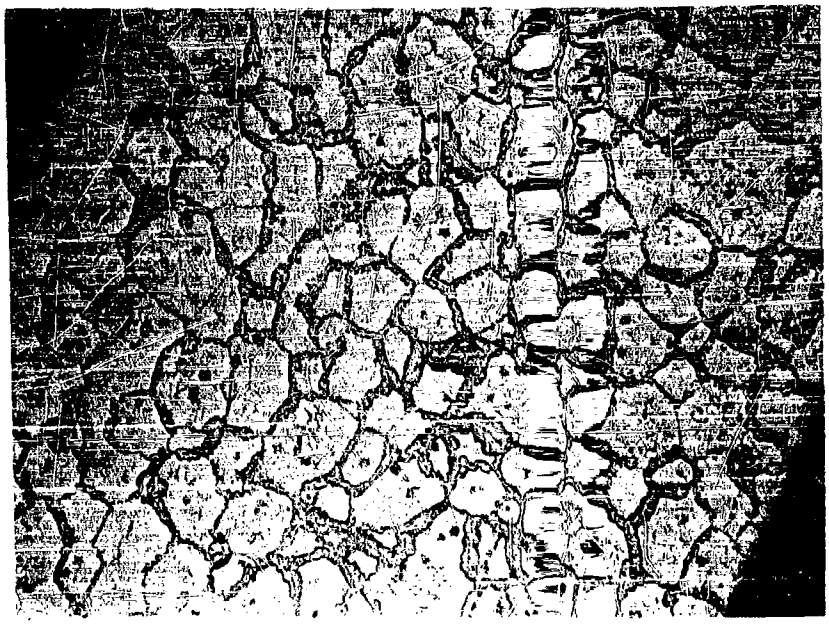

Fig. 11--Ta-6.3 Zr, 15 minutes at 2000°C, radiation quenched. 100X

Fig. 12--Ta-6.3 Zr, 1 hour at 2000°C, radiation quenched. 100X

Fig. 13--Ta-6.3 Zr, 16 hours at 2000°C, radiation quenched. 100X

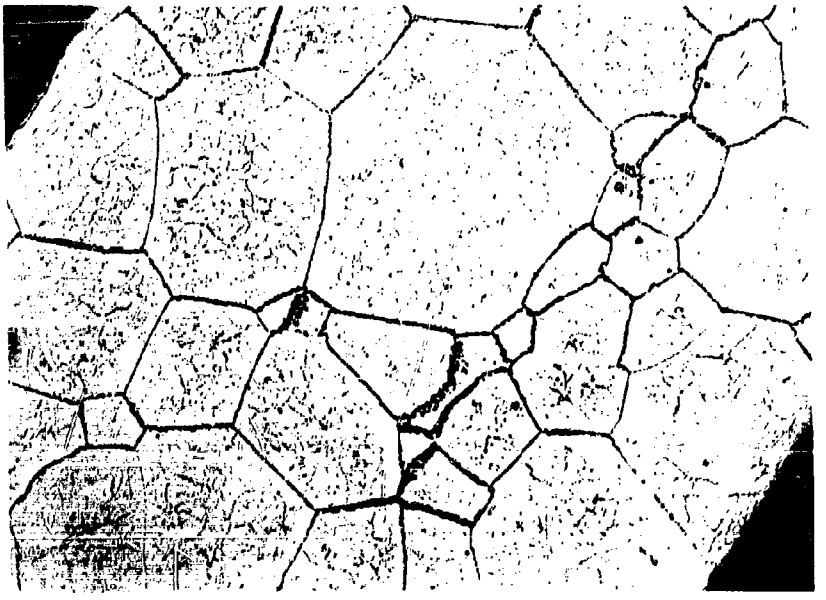

Fig. 14--Ta-6.3 Zr, 15 minutes at 2200°C, radiation quenched. 100X

Fig. 15--Ta-6.3 Zr, 1 hour at 2200°C, radiation quenched. 100X

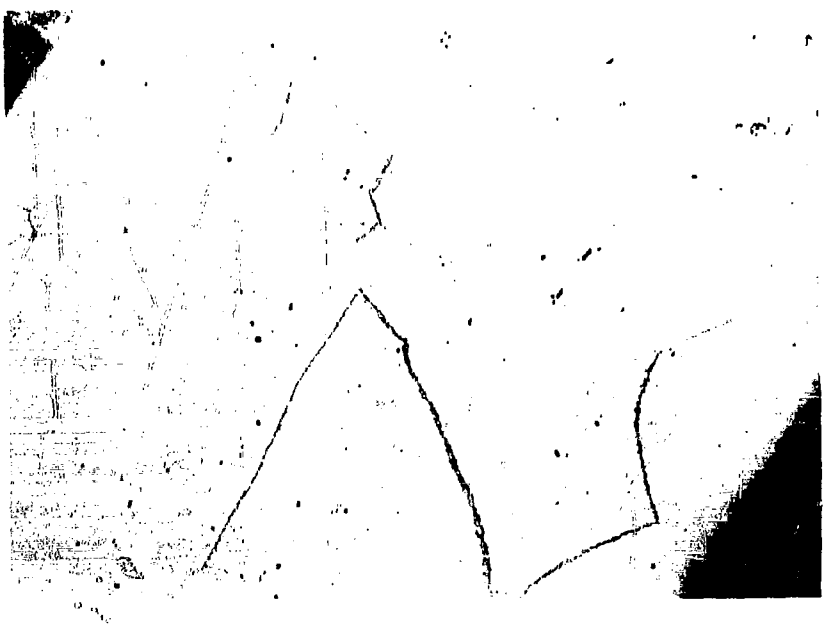

Fig. 16--Ta-6.3 Zr, 15 minutes at 2400°C, radiation quenched. 100X

Fig. 17--Ta-6.3 Zr, 1 hour at 2400°C, radiation quenched. 100X

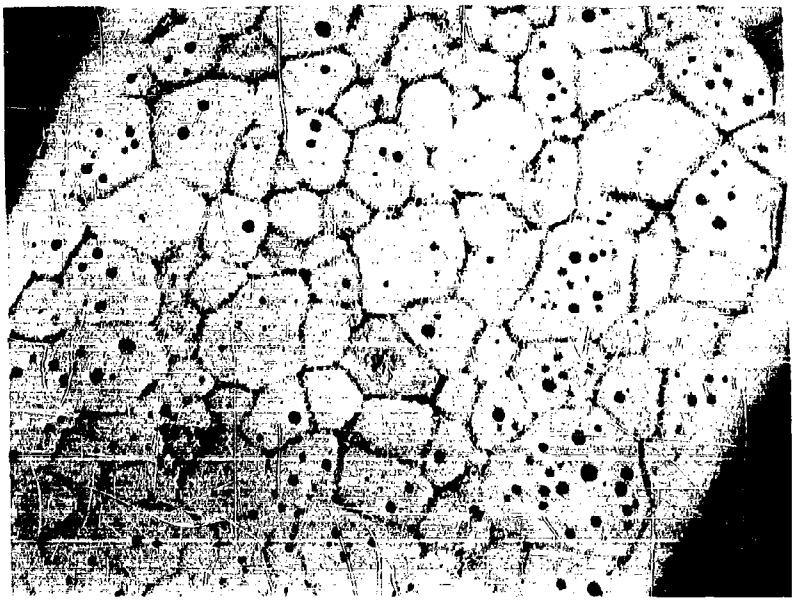

Fig. 18--Ta-6.3 Zr, 15 minutes at 2600°C, radiation quenched. 100X

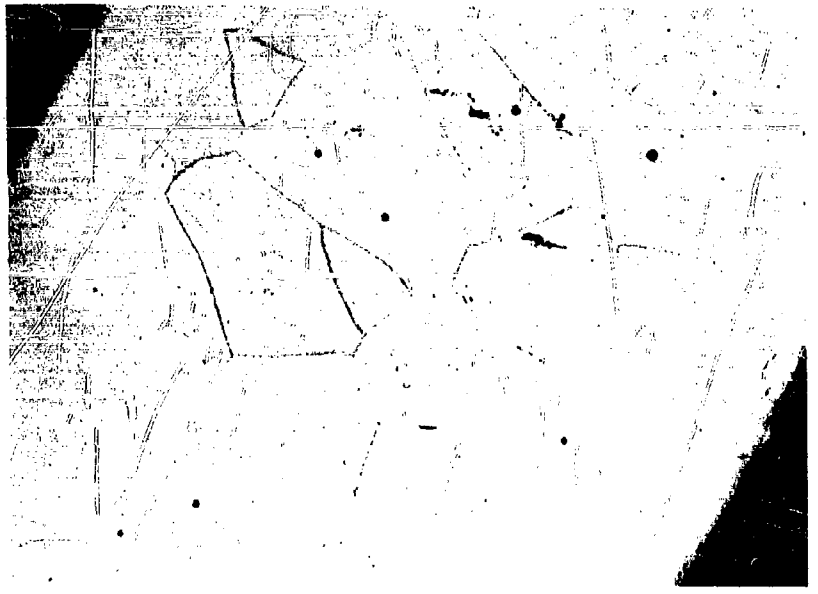

Fig. 19--Ta-6.3 Zr, 1 hour at 2200°C, pot quenched. 100X

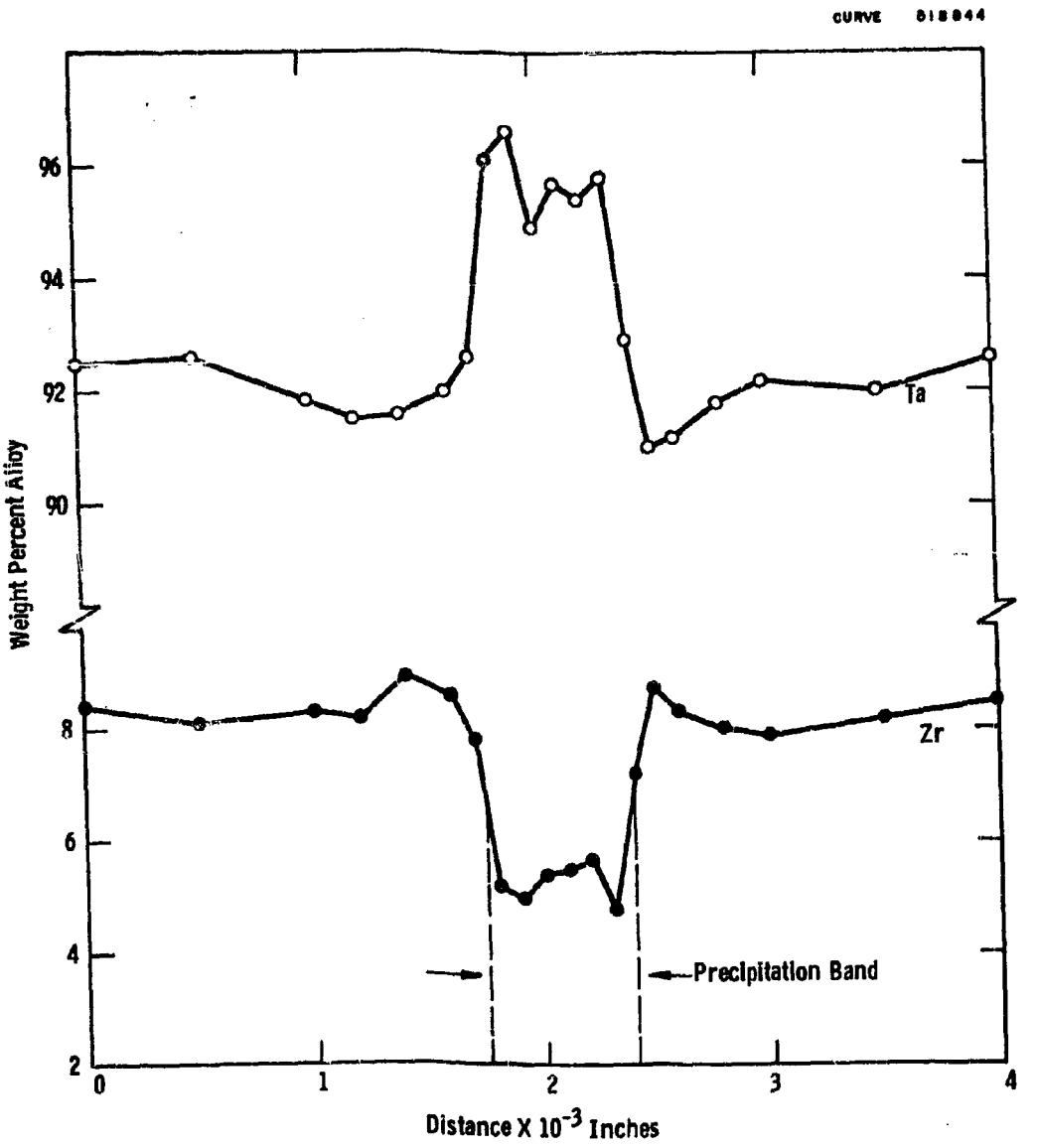

Fig. 20--Distribution of Zirconium and Tantalum across grain boundary containing a lamellar structure

TABLE III

EFFECT OF HEAT TREATMENT UPON HARDNESS OF Ta-6.3%Zr

Specimen Number	Treatment	Hardness (VHN)
470-5B	As rolled	287
470-9B	1 hr. 1800°C R.Q. *	309
470-5T	15 min. 2000°C R.Q.	301
470-4B	1 hr. 2000°C R.Q.	321
470-4B	16 hrs. 2000°C R.Q.	401
470-2B	15 min. 2200°C R.Q.	308
470-15T	1 hr. 2200°C R.Q.	353
470-14B	1 hr. 2200°C P.Q. **	325
470-15T	1 hr. 2200°C R.Q. 1 hr. 2200°C R.Q.	364
470-3T	15 min. 2400°C R.Q.	314
470-3T	15 min. 2400°C R.Q. 1 hr. 2200°C R.Q.	317
470-3B	1 hr. 2400°C R.Q.	318
470-11B	1 hr. 1800°C 1 hr. 2000°C 1 hr. 2200°C R.Q.	319
470-8T	1 hr. 2200 1 hr. 2000 1 hr. 1800 R.Q.	322
470-16T	1 hr. 2200°C P.Q. 1 hr. 2200°C P.Q.	260
470-16B	1 hr. 2200°C P.Q. 1 hr. 1450°C P.Q.	279
470-20B	1 hr. 2200°C P.Q. 1 hr. 1750°C R.Q.	321

* R.Q. - Cooled to black heat in about 2 min.

** P.Q. - Cooled to black heat almost instantly.

230 VHN compared to 500 VHN for an alloy annealed 15 minutes at 2000°C and radiation quenched. Annealing treatments below 1800°C had no consistent effect upon hardness. General precipitation during a 16 hour treatment at 1500°C reduced hardness as expected. Alloys cooled by the radiation quenching technique were harder than alloys pot quenched.

Discussion

The influence of heat treatment upon the properties of Ta-Zr alloys has not been definitely isolated. Behavior has been obscured by inhomogeneous structures, promoted by evaporation of Zr during heat treatment.

Further careful study is needed to definitely establish the Ta-Zr phase diagram. These data are needed to enable correlation between heat treatment, properties, and microstructure.

The usefulness of the aging reactions in these Ta-Zr alloys will probably by limited by several factors. The difficulties encountered in fabricating alloys containing 4 or more percent zirconium were apparently connected with the presence of the precipitate at the grain boundaries. Even worse, the marked precipitation and apparent overaging of the second phase at quite low temperatures indicates that it will not provide adequate stability for long time service at elevated temperatures.